

**Abiotic controls of fine sediment on the form and mobility of
phosphorus in a gravel-bed river during low flow**

by

Caitlin Watt

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Authors Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required revisions, as accepted by my examiners. I understand that this thesis may be made electronically available to the public.

Abstract

Landscape scale disturbance in forested source water regions can accelerate the transfer of fine sediment and associated phosphorus (P) to receiving streams and degrade water quality in downstream environments for human and ecosystem use. The abiotic controls of deposited riverbed and suspended fine sediment on the form and mobility of P were examined in an oligotrophic gravel-bed river undergoing cumulative downstream sediment pressures from disturbance (e.g., harvesting, wildfire and sewage effluent) in Alberta, Canada. The spatial distribution of particulate P forms (NAIP, AP, OP) and major element composition were assessed across six study sites in the Crowsnest River that receive tributary inputs from watersheds that have experienced a range of landscape disturbance types. Pore-water soluble reactive P (SRP) concentration profiles within the gravel-bed were measured with pore-water peepers. Diffusive fluxes from the sediment to the water column were related to landscape disturbances, substrate properties, dissolved oxygen concentrations, and fine sediment sorption characteristics. A series of batch experiments were conducted to determine the Equilibrium Phosphate Concentration (EPC₀) and evaluate the potential of fine sediment to influence P concentrations in the overlying water column. Results of the study demonstrated varying sensitivities to landscape disturbances due to the heterogeneous nature of gravel-bed substrate and morphology. Macro- to micro-scale processes influenced the form and mobility of P, however fine sediments in the riverbed irrespective of landscape disturbance demonstrated the potential of the riverbed to release SRP to the water column. Sewage inputs had the greatest impact on SRP fluxes from the riverbed and bioavailability of P in suspended sediments. The most bioavailable form of particulate P (NAIP) was associated with metal oxide and organic carbon coatings on sediment. Lower dissolved oxygen concentrations are likely responsible for driving the release of P from redox sensitive metals. Bioavailable particulate P and the release of SRP can influence in-stream water quality and ecological communities, and over longer time scales can propagate effects downstream to reservoirs and impact drinking water supplies. This thesis provides new knowledge regarding the impacts of both landscape disturbance and site-specific abiotic processes that influence the form and mobility of P in a gravel-bed river during the biologically sensitive period of summer low flow.

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Chapter 1

Introduction

1.1. Problem Statement

Phosphorus (P) is the limiting nutrient in freshwater ecosystems (Schindler, 1977; Bennett et al., 2001). Excessive additions of P from point and/or nonpoint sources can lead to eutrophication of aquatic systems that can have dramatic environmental and economic consequences (Carpenter et al., 1998; Correll, 1998; Mainstone & Parr, 2002). For example, increased P loading to receiving waters can accelerate the growth of macrophytic and periphytic vegetation (Reddy et al., 1999) and promote the growth of algal blooms (Heathwaite & Dils, 2000). The presence of cyanobacteria in these blooms can produce microcystins (Davis et al., 2009) which are toxic and pose a risk to drinking water supplies (Jones & Orr, 1994; de Figueiredo et al., 2004). Eutrophication can deplete oxygen levels in freshwater systems because of increased organic matter consumption by microbial communities (Bennett et al., 2001), which disrupts the trophic cascade within lake and reservoir systems (Correll, 1998). Furthermore, eutrophication can have negative impacts on drinking water supplies, industrial activities, tourism, fisheries, recreational economies, and property values (Sharpley et al., 1995; Bennett et al., 2001; Pretty et al., 2003; Dodds et al., 2009). As a result, there is great incentive to manage and protect freshwater resources against nutrient loading.

The majority of P from terrestrial sources entering streams is in particulate form (Krongvan et al., 1997), where particulate P (PP) is typically concentrated in finer sediment fractions due to the increased surface area of metal oxy-hydroxides coatings (Stone & Mudroch, 1989). Once PP enters receiving streams, it can strongly influence nutrient cycling within a river reach and in receiving waters downstream (Withers & Jarvie, 2008). The relationship between dissolved and particulate P forms in rivers is governed by a range of environmental and biogeochemical factors that influence the buffering capacity of sediment to control dissolved P in the water column via a reverse sorption process (Freolich et al., 1988; Walling et al., 1997; House, 2003). Accordingly, as sediment is transported as either suspended or bed load, the PP form and mobility are strongly

affected by sorption/desorption reactions in the river (Svendsen et al., 1995; Kronvang et al., 1997; Walling et al., 1997).

Fine sediment storage within riverbeds has been identified as the link between high flow delivery of sediments and low-flow release of SRP (House, 2003; Jarvie et al., 2005) because sediments within the riverbed can act as either sinks or sources of P to the water column (Owens & Walling 2002; Evans et al., 2004). Therefore, the deposition of sediment from high-flow events on the riverbed can impact the nutrient availability for ecological communities (Wood & Armitage, 1997), particularly during stable low-flow conditions (Jarvie et al., 2005). Indeed, depending on residence times of sediment within the riverbed, sediment deposition can lead to prolonged (legacy) effects of historic diffuse and point source disturbances (Walling et al., 2003; Jarvie et al., 2012; Sharpley et al., 2013; Powers et al., 2016). However, there is a knowledge gap regarding how riverbed sediments influence in-stream P cycling and quantification of fluxes from riverbeds (Jarvie et al., 2008; Withers et al., 2014). Furthermore, there is a need to attribute sources and forms of PP accurately in order to manage freshwater resources responsibly (Withers et al., 2014).

Sediment and aqueous geochemistry are factors that influence the distribution, type and bioavailability of PP (Reynolds & Davis, 2001). The various forms of PP are typically determined by sequential extraction techniques and defined operationally according to their ecological significance (Boström & Pettersson, 1982; Pettersson et al., 1988; Zhou et al., 2001). As a result, the risk of eutrophication is linked to the chemical composition of PP (Machesky et al., 2010; Peryer-Furdson et al., 2015). Non-apatite inorganic P (NAIP) is associated with labile P and P loosely bound to Al- and Fe- hydroxides (Pettersson et al., 1988), this PP composition is considered the most bioavailable (De Pinto et al., 1981). Other forms of PP including apatite P (HCl extractant) and organic P which can be important sources of P depending on aqueous chemistry and microbial communities (Nimick et al., 2011; Battin et al., 2016; Parsons et al., 2017). Particulate P forms are being recognized as an important measure in streams and rivers to address P loading and eutrophication (Pacini & Gächter, 1999; Withers et al., 2014; Peryer-Furdson et al., 2015).

The storage of P within riverbeds and the interaction of the water column and riverbed sediments of P cycling are important knowledge gaps in the literature (Jarvie et al., 2008). Moreover, there is limited quantification of pore-water P concentrations and sorption characteristics of riverbed sediment despite the fact that riverbed sediments have been reported to

be important for P retention and remobilization (Hendricks & White, 2000; Jarvie et al., 2005; Haggard et al., 2006). While much the research on sediment-associated P has focused mobilization from the terrestrial landscape (e.g., McDowell et al., 2002; Ellison & Brett, 2006; Ballantine et al., 2009; Emelko et al., 2016), there is a critical need to further explore how in-channel fine sediments contribute to the overall budget of P cycling in rivers (Owens & Walling, 2002; Stutter and Lumsdon, 2008; Withers et al., 2014).

Fine sediments have a strong affinity to bind dissolved P forms (Stone & English, 1993), and are important for the sorption/release of dissolved P to/from the water column in many aquatic systems (Froelich et al., 1988; van der Perk et al., 2006). The “zero equilibrium P concentration” (EPC₀) is the concentration at which a sample of known mass neither bind nor release P (Froelich et al., 1988). The ability of sediments to buffer P concentrations in the water column depends on a range of physical, chemical, and biological processes, such as particle size, specific surface area, redox conditions, pH, geology, biofilms and micro-niches (Woodruff et al., 1997; Stone & English, 1993; Katsev et al., 2006; Stockdale et al., 2009). EPC₀ has been used as an indicator to identify critical areas of in-stream nutrient loading (Palmer-Felgate et al., 2009; Rawlins, 2011; McDowell et al., 2015a). Despite the potential use of this indicator relatively few studies have been conducted to examine the spatial and temporal variability of EPC₀ for sediments in rivers.

The understanding of riverbed P dynamics and the influence on water column concentrations are increasingly being studied (e.g., Gainswin et al., 2006; Jarvie et al., 2008; Burns et al., 2015; Fitzgerald et al., 2015). However, most research has focused on agricultural and urban impacts in fine-grained riverbeds (e.g., Ballantine et al., 2006; Rawlins, 2011; Son et al., 2015). The eastern slopes of the Rocky Mountains are important forested source water regions for water supply and historically these regions have been oligotrophic (Emelko et al., 2016). Increasing landscape disturbance from anthropogenic disturbances and climate change are putting pressure on the water quality of these systems (Silins et al., 2014; Emelko et al., 2016). Furthermore, there is limited knowledge of how P dynamics shift downstream with differing tributary inputs of sediment, their cumulative effects, P processes within gravel-bed rivers (Chambers et al., 1992; Vervier et al., 2009) and the effects of fine sediment within the gravel-bed matrix (Koiter et al., 2015). Biogeochemical cycling of P is affected by land-use, catchment characteristics, geology, and point sources (McDowell et al., 2002; Ellison & Brett, 2006; Jarvie et al., 2006; Ballantine et

al., 2009; Palmer-Felgate et al., 2010). A better understanding of the complexity of P cycling is necessary for proper and effective resource management (Kerr et al., 2011).

1.2. Literature Review

1.2.1. Phosphorus in aquatic ecosystems

Phosphorus (P) is the limiting nutrient in freshwater aquatic ecosystems and increased levels of P can significantly increase growth of algae, periphyton, and biofilms (Schindler, 1977; Tilman, 1982; Lewis et al., 2011), which can cause shifts in ecological communities and negatively impact the health of aquatic ecosystems (Bennett et al., 2001). Eutrophication is defined as nutrient enrichment in aquatic ecosystems related to elevated phosphorus concentrations from diffuse and point sources that cause nuisance algal blooms (Correll et al., 1998), reduce water quality and impact drinking water supplies (Carpenter et al., 1998; Jarvie et al., 2006; Emelko et al., 2011). Algal blooms suppress light penetration into the water column and limit the ability of other organisms to photosynthesize (Kirk, 1994). Furthermore, microbial decomposition of organic matter consumes oxygen which when coupled with reduced photosynthetic activity can create an anoxic environment, harming habitat and stream health (Harper, 1992). Cyanobacterial blooms are of particular environmental and human health concern as they can produce toxic microcystins (Davis et al., 2009), which have been acknowledged as a potential source of harmful by-products during treatment (Jones & Orr, 1994). Overall, P loading in aquatic ecosystems can have detrimental impacts on water quality (Orihel et al., 2017) and water treatability (Emelko et al., 2011).

Dissolved and particulate forms of P can be utilized by biota in aquatic ecosystems and the availability of both forms can lead to shifts in trophic status of water bodies (Reynolds & Davis, 2001; Withers & Jarvie, 2008). Dissolved P or soluble reactive P (SRP) in the water column are operationally defined as P that can be passed through a 0.45 μm filter, while particulate P (PP) is the residue left on the filter (Holtan et al., 1988). Dissolved P is typically more bioavailable, while particulate P forms can either retain or release SRP (Froelich et al., 1988; Reynolds & Davis, 2001). A significant body of research has focused primarily on how sediments buffer dissolved P concentrations in the water column (e.g., Klotz, 1988; Reddy et al., 1995; McDowell and Sharpley, 2003; Li et al., 2016). Much of this research has been directed towards understanding how diffuse

P sources, such as agriculture, transfer PP forms from the landscape to receiving streams (e.g., Ellison & Brett, 2006; Ballantine et al., 2009). The interplay between particulate and dissolved forms of P in aquatic systems is controlled by a complex set of environmental factors such as hydrology, geology, morphology and land-use (House & Denison, 2002; Doyle & Stanley, 2003; Evans et al., 2004). Particulate P stored in the riverbed and on the floodplains can be remobilized and therefore can influence the interaction of PP and SRP, which is dependent on antecedent conditions (House, 2003). In addition, the ability of PP to desorb SRP, and the bioavailability of PP, will depend on sediment sources that reflect surrounding geology (Ballantine et al., 2009) and land-use (Stutter & Lumsdon, 2008). Accordingly, the form and availability of P in the water column will depend on the source of particulate matter, catchment characteristics and the dynamics between abiotic and biotic transformations of P (Reynolds & Davis, 2001; Withers & Jarvie, 2008).

1.2.2. Landscape disturbance impacts on sediment and phosphorus

Globally, forested catchments are recognized as an important resource for the maintenance of water quality, ecosystem health and drinking water treatability (Ice & Binkley, 2003; Allan et al., 2004; Bladon et al., 2014). However, it is increasingly recognized that a range of natural and anthropogenic landscape scale disturbances have negatively impacted water supply and quality in forested regions (Farber et al., 2002; Stein & Butler, 2004). With increased environmental pressures from urbanization, agriculture, and climate change related impacts (e.g., drought, insect infestation, wildfire), there is a growing body of literature that has identified the need to examine the interplay between land disturbance type, sediment sources, P mobility and P propagation in aquatic systems (e.g., Sharpley et al., 2013; Stone et al., 2014; Pistocchi et al., 2017). Historical loading of P to water bodies has created a legacy effect (Sharpley et al., 2013) where sediments have been shown to release P when external P loads are reduced (Sondergaard et al., 2001). Moreover, few studies have assessed cumulative effects of multiple land-uses, particularly in systems that are historically oligotrophic (Smith & Owens, 2014) and are undergoing increasing pressures, leading to uncertainty in ecosystem responses. In order to responsibly manage water resources in the long term, there is a critical need to better understand how current and historical land-use affect P dynamics and recovery times in aquatic systems (Meals et al., 2010).

In the literature, there has been a primary focus on anthropogenic disturbances such as agriculture and urban development on P cycling (McDowell et al., 2001; Owens & Walling, 2002; Hoffman et al., 2009; Sharpley & Wang, 2014; Cooper et al., 2015). Harvesting and climate-driven disturbances such as wildfire have been studied to a lesser extent with respect to P cycling (e.g., Burrows et al., 2013; Hawthorn, 2014; Emelko et al., 2016). Landscape disturbances can influence mobility, transport and fate of sediment and associated phosphorus as they modify hydrological and biogeochemical processes (Kreutzweiser & Capell, 2001; Son et al., 2015; Emelko et al., 2016), these effects can last over range of time scales depending on the geology, hydro-climatology and vegetation type in a watershed. An accurate representation sediment and P sources are needed in order to correctly identify areas of concern and manage landscapes effectively (Withers et al., 2014), particularly given the complex nature of sediment sources (Collins et al., 2002). Furthermore, the understanding of the biogeochemical processes that bind and release P to and from particulate matter will provide further insight into catchment specific responses to landscape disturbances and better inform management decisions.

Point and diffuse sources of P are primarily attributed to wastewater (sewage and industrial) and agricultural runoff, respectively (Bowes et al., 2005; Jarvie et al., 2006; Kronvang et al., 2007; Jarvie et al., 2006). In addition, some argue that agriculture is the largest contributor to eutrophication (e.g., Carpenter et al., 2005). Specific land use types that tend to increase soil erosion are significant for P transfer to the waterways (e.g., Haygarth et al., 2005; Silins et al., 2009). Sources of P from agricultural landscapes are typically associated with surface and tile drain runoff, the contribution of each depends on hydro-climatic variability, slope, soil type, crop type and antecedent moisture conditions (Macrae et al., 2007; Lam et al., 2016). Wastewater inputs of P from sewage treatment P depend on treatment and the size of the “sewered population” in a catchment (Withers & Jarvie, 2008). Furthermore, impacts of harvesting have been shown to increase sediment and nutrient concentrations in receiving streams (Martin et al., 2000; Kreutzweiser et al., 2008). Climate-change is causing increases in landscape disturbances that threaten ‘green infrastructure’ which ensure high quality drinking water supplies (Emelko et al., 2016). For instance, wildfire is a major threat to water supplies as this rapid landscape change can supply significant amounts of sediment and associated nutrients from terrestrial surfaces into rivers and lakes (Silins et al., 2009; Blake et al., 2010). P loading due to wildfire can differ significantly and depending on catchment characteristics the persistence of effects can span longer time scales.

Different land-uses and geologies can significantly influence the ability of sediments to bind P (Ballantine et al., 2009), which ultimately influence the transportation and transformation of P.

In-stream biogeochemical processing is a critical consideration for land-use management as bed sediment retention and remobilization can confound the apportionment of landscape disturbance impacts (Withers & Jarvie, 2008; Jarvie et al., 2012). Furthermore, in rivers which are less ‘flashy’ increased in-stream processing can occur with greater retention and residence times (Basu et al., 2011). Retention of sediments in streams and the dynamic nature of P cycling makes cumulative assessments difficult as nutrients can be temporally stored within a reach. In addition, differences in the physical and chemical composition of riverbed material can vary with historical land-use, which leads to a diverse set of ecological responses (Sharpley et al., 2014). The propagation of sediment downstream, can lead to changes in biogeochemical processes and P availability (Kronvang et al., 1997), which can cause shifts in ecological assemblages and water quality (Wood & Armitage, 1997). Overall, the assessment of cumulative effects is complicated by retention of sediment within the riverbed, historical inputs and dynamic changes of P during transportation.

1.2.3. Phosphorus cycling in rivers

Storm flow events can provide significant fluxes of sediment and P (Abell et al., 2013) capable of transporting a large proportion of annual P loads (Haggard et al., 2006), also remobilization of riverbed sediment can propagate nutrients downstream (Koski-Vähälä & Hartikainen, 2000; Evans et al, 2004). Fine sediments typically have higher P content (e.g., Stone & English, 1993; Zhang & Huang, 2007) compared to coarse materials, their small size and low settling velocity often result in fine sediments being transported long distances in rivers (Haralampides et al., 2003). Furthermore, the geochemical composition of particulate matter is dynamic and availability of P has been seen to change during sediment transportation (Ballantine et al., 2009). The transport of sediment potentially enriched with P has implications for downstream waterbodies (Svendsen et al., 1995; Kronvang et al., 1997). The deposition of sediments and associated P in a riverbed following a high flow event may contribute P fluxes to the overlying water during low flows when P is released from sediment to the water column (Owens & Walling, 2002). Additionally, abiotic

and biotic uptake and release of sediments can influence the downstream transport of P (Taylor & Kunishi 1971; Newbold et al., 1983).

Elevated sediment-associated P fluxes from watersheds are typically associated with increasing levels of disturbance (Palmer-Felgate et al., 2009; Wohl, 2015). However, very little is known about how fine sediment is stored in gravel-bed streams and the short- and long-term impacts of sediment on dissolved P concentrations in the water column during low flow. In some rivers the water column concentrations may be elevated enough to allow for the uptake of P by river sediments. Conversely, in stream reaches with low P concentrations in the overlying water coupled with saturated sediments, the increased release of P to the water column may occur. While sediments in aquatic ecosystems are recognized for their ability to buffer SRP (e.g., Froelich, 1988; Stone & Murdoch, 1989; Evans et al., 2004; Lottig & Stanley, 2007), very little is known about the abiotic control of fine sediment on P mobility in gravel bed rivers (Karna et al., 2014). In addition, bed characteristics such as particle size can affect the fate of sediment-associated P inputs to streams by trapping fine sediment (Bonvallet et al., 2001; Karna et al., 2014). Understanding the role of riverbeds as potential sinks/sources of phosphorus should help improve the understanding of P transport and spiraling, as well as provide better context for river management (Svendsen et al., 1995; Withers & Jarvie, 2008).

1.2.4. Particulate phosphorus forms and sediment geochemistry

The transport and storage of sediment-associated P can impact the ecological status of rivers and streams, particularly with biologically available forms of particulate P (Krongvang et al., 2003). Operationally defined sequential extractions of particulate P can be used to evaluate the bioavailability of particulate P which is associated with the risk of eutrophication (Pettersson et al., 1988; Katsaounos et al., 2007; Meng et al., 2014; McDowell & Hill, 2015). Extraction techniques have been developed and modified from the initial work of Chang and Jackson (1957) to more accurately characterize sediments with aluminum, iron and manganese oxides and hydroxides, calcium and organic/humic components (e.g., Williams et al. 1967; Hielajes & Lijkla 1980; Psenner et al., 1984). Non-apatite inorganic phosphorus (NAIP) is generally associated with metal hydroxide surfaces and considered a bioavailable form of particulate P (Emelko et al., 2016). Others define Fe-bound or NaOH extractable (one of the three NAIP leaches) as ‘algal available’

(e.g., De Pinto et al., 1981; Lottig & Stanley 2007). Following the method of Psenner and Istvanovics (1988) NAIP is determined as the sum of three leaches [NH_4Cl (1.0M), BD (0.11M, 40°C) and NaOH (1.0 M)]. Other particulate forms include apatite phosphorus (AP) determined with HCl (0.5M) leach and this form is considered to be geochemically stable. Organic phosphorus (OP) is determined using a NaOH (1.0M, 85°C) leach and is considered potentially available because it can be mineralized or released with hydrolysis (Golterman, 2004). Overall, PP forms differ in bioavailability and therefore differentially contribute to the risk of eutrophication. Accordingly, failure to monitor PP forms can create uncertainty regarding eutrophication (van der Grift et al., 2018).

Iron, manganese and organic matter coatings on the surface of particulate matter have been correlated with total PP concentrations (Evans et al., 2004). Redox conditions change the binding of aluminum, iron and manganese to mineral surfaces and humic substances (Mortimer, 1941; Borch et al., 2010). Anaerobic conditions allow for the reduction of iron oxy-hydroxides and the hydrolysis of organic phosphorus (Löfgren & Boström, 1989; Jensen et al., 1992; Golterman, 1995; Ruttenberg & Sulak, 2011). The iron oxy-hydroxide (and other metals) acts as an electron acceptor to the phosphate ion that has a high negative charge thus causing the phosphate ion to sorb to the metal complex. Additionally, metal transformations can modify the availability of P and significantly contribute to fluxes of P (Klotz, 1991). Changes in the availability of metal oxy-hydroxides will influence labile P bound to metal coatings on sediments, with fewer available metal oxides likely resulting in less sorption to sediments (Golterman, 2004).

Abiotic uptake and release of P in rivers is driven by sorption/desorption reactions and precipitation/dissolution reactions (Withers & Jarvie, 2008). Sorption/desorption reactions are dependent on environmental conditions, such as pH and redox, as well as competing organic matter complexes (Reddy et al., 1999). Organic matter is another contributor to the adsorption of phosphorus (McDowell et al., 2001; House & Denison, 2002). Precipitation and dissolution reactions are usually due to quick changes in pH (Aminot & Andrieux, 1996), precipitation of P with calcite may be facilitated by biota during photosynthesis (Neal et al., 2001). In anoxic environments, SRP can precipitate with iron and calcite to form relatively stable P compounds (Golterman, 2004). Geochemical controls of P are considered to play a significant role in P availability (Bostrom et al., 1988; van der Perk et al., 2006), however the availability of metals, calcite and organic carbon is not only driven by catchment sources but by chemical gradients that

can be created due to the presence of biofilms (Boano et al., 2014). Many researchers point to the importance of macrophytes, benthic communities and phytoplankton for P cycling and retention (e.g., Kleeberg et al., 2010; Battin et al., 2016). Consequently, abiotic and biotic transformations are coupled, both influencing each other and the dynamic nature of PP forms.

Particulate P forms have largely been studied in marine and lentic environments (e.g., Bostrom et al., 1988; Andrieux-Loyer & Aminot, 2001; Purushothaman & Chakrapani 2015), with limited information on PP forms in lotic systems (van der Grift et al., 2018). Within lotic systems, a broad range of PP forms and P content have been observed. For example, P content in riverbed sediment in Mahantango Creek, Pennsylvania, was $\sim 200 \text{ ug g}_{\text{sed}}^{-1}$ (McDowell & Sharpley, 2003), while Noll et al. (2009) found P content to be a magnitude larger, $\sim 2000 \text{ ug g}_{\text{sed}}^{-1}$ in Graywood Gully, New York, both catchments dominated by agriculture. Moreover, the forms of PP in riverbed sediments can change within the same river, Barral et al. (2012) found that riverbed PP in the Anllóns River (NW Spain) that urban impacts differed with different surround geologies. The form of PP can vary seasonally and by stream order (e.g., Fogal et al., 1995) as a function of variable source area and streamflow. De Pinto et al. (1981) observed that the amount of bioavailable P in suspended sediments from tributaries of the Great Lakes differed between Ohio and New York, with the former having higher amounts of NAIP. Varying amounts of PP forms in lotic systems are likely a result of different morphology, sediment sources, site specific geology and water chemistry, as well as the downstream transformations of PP forms (Stone & Mudroch 1989; Reddy et al., 1999; Hendricks & White, 2000; Katsev et al. 2006; Records et al., 2016). More research is needed to better understand how different landscape disturbances and downstream propagation influences the spatial and temporal variability in PP forms (van der Grift et al., 2018).

1.2.5. Phosphorus mobility

The release/uptake of P from/to sediments occur in a two-step process; first, surface adsorption that occurs rapidly then a slow ‘solid-state diffusion’ (Froelich, 1988). The ability of sediment to buffer P from solution is typically determined using P isotherm experiments and sorption models (e.g., Langmuir, Freundlich, Tempkin). The ability of sediments to adsorb or desorb P can be examined through the maximum adsorption capacity of sediment or the solution

concentration at which neither adsorption or desorption occurs, known as the ‘zero equilibrium concentration’ (EPC₀) (Froelich, 1988). The EPC₀ is typically determined using a series of SRP concentrations mixed with a known mass of sediment for sufficient time that equilibrium between the sediment and solution can be assumed (Golterman, 2004). The data are then fitted with initial concentration on the x-axis and P absorption/desorption on the y-axis, calculated by equation 1.1.

$$P_{ads} = [(P_{initial} - P_{final}) * 0.025L] * wt_{sed}^{-1} \quad (1.1)$$

The slope of the buffer diagram at EPC₀ represents the adsorption coefficient; steep slopes represent greater ability to buffer P (Froelich, 1988). Buffer diagrams are used to examine mechanistic behavior of sediments (Froelich, 1988). However, solution pH, ionic strength, temperature, ratio of sediment to solution and solution chemistry can all influence the sorption characteristics (Klotz, 1988; Lucci et al., 2010; Bhadha et al., 2012), therefore results from sorption studies (P isotherms) cannot be directly translated to the ecosystem, but can provide a relative proxy (Barrow, 1983). Moreover, sorption characteristics are dependent on physical, chemical and biological conditions of the riverbed (Valett et al., 1996; Mullholland et al., 1997; Katsev et al., 2006; Battin et al., 2008), therefore coupling a better understanding of sorption with in-stream and streambed biogeochemical processes is necessary to understand P release.

EPC₀ concentrations for riverbed sediments vary widely across the literature and even within the same study (Table 1.1). In the wildfire impacted Cache la Poudre River, Colorado, Son et al. (2015) found the sediment EPC₀ ranged from 300 and 1200 µg L⁻¹. Due to the complexity of P sorption to particulate matter there can be a wide range of results even when assessing a single land-use. EPC₀ concentrations associated with agriculture land-use can range from as low as 100 µg L⁻¹ (McDowell and Sharpley, 2003; Hoffman et al., 2009; Palmer-Felgate et al., 2009; Machesky et al. 2010) to values >1300 µg L⁻¹ (Agudelo et al., 2011). House and Denison (2002) found EPC₀ concentrations as high as 610 µg L⁻¹ in River Blackwater, England, while Wang and Pant (2010) observed EPC₀ concentrations as high as 730 µg L⁻¹ in the Bronx River, New York, both examples of rivers impacted by wastewater inputs. The variability of EPC₀ of riverbed sediments can be attributed to different sediment sources and activated source areas (Stutter & Lumsden, 2008), sediment geochemistry (Hartikainen et al., 2010; Rawlins et al., 2011), and land-use (Stone & English, 1993). To date, no research has been conducted to examine the variability of EPC₀ within a gravel-bed river across a single season within the same reach and along a gradient of differing landscape disturbances.

Table 1.1. - EPC₀ concentrations ($\mu\text{g L}^{-1}$) for different riverbed sediments across a variety of landscapes and impact

Citation	Location	Impacts	Site	Min EPC₀	Max EPC₀
This study	Alberta, Canada	Wildfire, sewage	Crowsnest River	41	579
Klotz 1988	New York, USA	Headwater	Hoxie Gorge Creek	<1	2
Stutter and Lumsdon 2008	NE Scotland	Moorland, bog, grassland, forest plantations	River Dee	1	54
Reddy et al. 1996	Florida, US	Dairy farms/pasture	Otter Creek	120	230
McDowell and Sharpley 2003	Pennsylvania, USA	Majority agriculture	Manhantango Creek	11	39
Jarvie et al. 2005	SW UK	Agriculture, pasture, grazing	Avon	2	178
Jarvie et al. 2005	SW UK	Agriculture, pasture, grazing	Wye	<1	195
House and Warrick 1999	NE England	Pasture, tributary with sewage impact	Swale River	1	55
Palmer-Felgate et al. 2009	Southern UK	Differing agricultural intensity	Avon/Wye/Welland	2	79
Hoffman et al. 2009	Wisconsin, USA	Agriculture	Dorn Creek	6	71
Machesky et al. 2010	Illinois, USA	Agriculture	Spoon River	6	68
Agudelo et al. 2011	Kansas, USA	Intensive agriculture	Upper West Emma Creek/Red Rock Creek	800	1300
Ekka et al. 2006	Arkansas, USA	WWTPs, agriculture, pasture	Illinois River	<10	290
House and Denison 2002	Southern UK	Sewage	River Blackwater	6	610
Wang and Pant 2010	NY, USA	WWTP, stormwater, urban	Bronx River	20	730
McDowell et al. 2015	New Zealand	Differing impacts	National scale study (76 sites)	7	100
Son et al. 2015	Colorado, USA	Wildfire	Cache la Poudre River	300	1200

1.2.6. Phosphorus transformations in the hyporheic zone

The hyporheic zone is defined as the ecotone between the water column of a stream and groundwater, where the hydrological exchange in the hyporheic zone has implications for riverbed and watershed nutrient spiraling (Ensign & Doyle, 2006; Lapworth et al., 2011; Harvery & Gooseff, 2015). Hyporheic flow paths disproportionately contribute to chemical reactions at the reach scale (Marzadri et al., 2012), which can provide transformations that increase the bioavailability of P (Brunke & Gosner 1995; Findlay, 1995; Assegid et al., 2015). For instance, Pepin and Hauer (2002) found that upwelling zones were hotspots for nutrient release and therefore algal growth. Groundwater generally has less oxygen than surface waters creating a chemical gradient in oxygen and therefore redox conditions (Boano et al., 2014). Furthermore, geochemical signatures of ground and surface water can be distinct (i.e. conductivity, pH, temperature, etc.), thus there are different preferential chemical transformations and distinct chemical gradients across the hyporheic zone (Boulton et al., 1998). The relative contribution of groundwater fluxes to the stream during low flow may provide significant P fluxes due to geochemical differences in groundwater and surface water (Dupas et al., 2015). While the hyporheic zone is considered an important zone for nutrient transformation (Triska et al., 1993; Findlay, 1995; Bardini et al., 2012), few studies have directly measures P dynamics in the hyporheic zone of rivers and even fewer in gravel-bed rivers (e.g., Jarvie et al., 2008; Vervier et al., 2009).

1.3. Research objectives

The goal of this research is to examine the abiotic control of fine sediment on phosphorus form and mobility by fine sediment in a gravel bed river during the environmentally sensitive period of summer low-flow. The spatial distribution and variation (inter- and intra-site variability) of PP forms (NAIP, AP, OP) and P mobility (EPC_0) were determined and related to the geochemical composition of sediment and environmental factors (dissolved oxygen, temperature, SRP concentrations in pore-water and the water column) in the Crowsnest River AB. The study was designed to examine the cumulative downstream impacts of land disturbance pressures (roads, harvesting, wildfire, and urban impacts – i.e., sewage effluent) on PP form and mobility. The main objectives of this work were:

1. Examine inter- and intra-site variability of PP forms (NAIP, AP, OP) in fine sediment (suspended and riverbed) as a function of sediment geochemical properties and landscape disturbance.
2. Determine the downstream effects of fine sediment on pore-water SRP concentrations in gravel-bed and estimate the SRP fluxes across the sediment-water interface.
3. Assess inter- and intra-site variability in P mobility (EPC_0) of fine sediment along a downstream gradient of landscape disturbance pressures.

1.4. Thesis Format

The Problem Definition, Literature Review and Thesis Objectives are provided in Chapter 1. The examination of riverbed and suspended PP forms relative to landscape disturbance, geochemistry and physical properties are addressed in “Geochemical composition and phosphorus speciation of deposited and suspended fine sediment in a gravel-bed river” (Chapter 2). Pore-water P concentrations and P sorption characteristics of fine sediment in the riverbed are addressed in “Abiotic control of fine sediment on P dynamics in gravel-bed rivers” (Chapter 3). Chapter 4 provides a synthesis of conclusions and addresses particulate P form and mobility relative to each other.

Chapter 2

Geochemical composition and phosphorus speciation of riverbed and suspended fine sediment in a gravel-bed river

2.1. Summary

Sediment plays a significant role in regulating both the form and bioavailability of phosphorus (P) in many river systems. Several studies have been conducted in rivers impacted by urban and agricultural land use, much less is known about P dynamics in typically oligotrophic forested source water regions undergoing sediment pressures from natural and anthropogenic land disturbance pressures. Furthermore, few studies have specifically examined the abiotic control of fine sediment on particulate P (PP) form in gravel-bed streams. In this study, the spatial distribution of major elements and PP forms (NAIP, AP, OP) in riverbed and suspended fine sediments were determined to examine landscape disturbances effects on PP form and bioavailability during environmentally sensitive conditions of low-flow. Study sites were selected in reaches of the Crowsnest River, Alberta, Canada and were located downstream of tributary inflows that represent pressures from a range of land disturbance pressures (e.g., roads, harvesting, wildfire, sewage effluent). The data show an increase in the percentage of bioavailable PP (NAIP) with sewage inputs which had the strongest impact and riverbed locations with reduced permeability. Results were confounded by the scale of disturbance and the difficulty in apportioning changes in PP form and mobility to specific landscape impacts, as well as variation in the size of riverbed substrate and channel morphology. Suspended sediment had higher concentrations of bioavailable and organic PP forms relative to fine riverbed sediments. Metal-oxy-hydroxides, LOI and organic carbon content were all higher in suspended compared to riverbed fine sediment. Manganese oxide and organic carbon were strongly correlated with changes in biologically available P (NAIP) in the Crowsnest River. Overall, inter- and intra-site variability of PP forms reflected differences in landscape disturbances, geochemical properties of sediment and local environmental conditions, demonstrating the dynamic nature of P availability in gravel-bed rivers and the difficulty in assessing and managing landscape disturbances.

Key words: Fine sediment; channel bed sediment; suspended sediment; particulate phosphorus forms; major element composition, gravel-bed rivers

2.2. Introduction

In forested source water regions, natural and anthropogenic landscape disturbances can significantly modify hydrology, sediment transport and nutrient dynamics (Allan et al., 2004; Silins et al., 2009), which can have long lasting impacts on water quality and nutrient dynamics in river systems (Wohl, 2015; Emelko et al., 2016). In North America, high quality water is generated from forested regions along the eastern slopes of the Rocky Mountains, however sediment and associated phosphorus fluxes generated from increasing landscape disturbance pressures have been shown to impact water drinking water supply (Emelko et al., 2011) and aquatic ecology (Silins et al., 2014). Phosphorus (P) is the limiting nutrient in freshwater aquatic systems (Schindler, 1977) and an excess of P can lead to eutrophication and nuisance algal blooms (Correll, 1998; Withers & Jarvie, 2008). Phosphorus is primarily associated with sediments (Kronvang et al., 1997), which are transported and cycled downstream in rivers (Logan et al., 1982; House 2003). Specifically, fine sediments contribute significantly to P cycling (Dorioz et al., 1989; Stone & English 1993; Zhang & Huang, 2007). Landscape disturbances can accelerate the supply sediment and associated phosphorus to rivers, which can ingress into riverbeds (Beschta & Jackson, 1979; Karna et al., 2015) thus affecting legacy impacts of P (Jarvie et al., 2005).

High flow events can produce bed shear stresses sufficient to mobilize the gravel bed armour layer, thus releasing fine sediment and associated P to the water column (Evans et al., 2004; Haygarth et al., 2005). The subsequent mobilization and downstream transport of fine sediment can influence microbial and algal productivity in receiving waters (Bostrom et al., 1988; Wood & Armitage 1997; Emelko et al., 2016). The majority of research on particulate P forms in riverine systems has focused on sediment-associated P during high flows where significant transport of P occurs (e.g., McDowell & Sharpley, 2002; Kerr et al., 2011). However, there is an increasing appreciation of the importance of internal cycling of P during biologically critical periods, such as low flow (House & Warrick, 1999; Jarvie et al., 2005; Stutter & Lumsdon, 2008). During low flow conditions, fine riverbed sediment can act as either a source or sink of P to the water column (Jarvie et al., 2005), which can affect aquatic ecology (Mulholland et al., 1997; Boulton et al., 2010).

In aquatic systems both the concentration and form of particulate P (PP) can vary spatially and temporally due to differences in land use, geology, vegetation, soil type and hydro-climatic variability (Owens & Walling, 2002; Katsaouous et al., 2006; Katsev et al., 2006). Some studies

have examined differences in the temporal and hydrological changes in PP form and governing mechanisms controlling P dynamics in riverbed sediment (e.g., Stone & English, 1993; Katsaounos et al., 2007; Ballantine et al., 2009) and suspended sediment (e.g., Emelko et al., 2016). Mechanisms that govern sediment P adsorption vary according to sediment type (suspended vs. riverbed; e.g., Cooper et al., 2015), morphology (Hendricks & White, 2000), redox conditions (Records et al., 2016) and mineralogy (Stone & Murdoch, 1989). Cumulative land-use effects on P cycling in streams are poorly understood, particularly those in forested watersheds that have historically been oligotrophic (Smith & Owens, 2014). Previous studies show that it is difficult to directly compare results from catchments with different geology, sediment mineralogy and soil type (Records et al., 2016) and there is a need to how drivers of P release change downstream in response to multiple landscape pressures.

Physical, chemical and biological factors that govern the form and availability of P have been extensively studied in lacustrine (e.g., Bostrom et al., 1988; Purushothaman & Chakrapani 2015), marine (e.g., Andrieux-Loyer & Aminot, 2001) and sand/silt riverine environments (e.g., Stone & English, 1993; Fogal et al., 1995; Ballantine et al., 2009; Peryer-Fursdon et al., 2015) but limited nutrient cycling research has been conducted on gravel-bed river systems (e.g., Gainswain et al., 2006; Vervier et al., 2009). Iron, manganese and calcium can exert strong geochemical controls on the form and availability of sediment-associated P (Golterman, 1988; Jensen et al., 1992; Katsev et al., 2006) but the extent to which these elements govern P form differ between catchments and redox environments (Records et al., 2016). The binding of P to iron and manganese are largely driven by redox conditions (Evans et al., 2004). In alkaline systems, calcium and magnesium play a more significant role in P binding (Golterman, 1988; House & Denison, 1992). While hyporheic zones have been identified as important for biogeochemical cycles (e.g., Bardini et al., 2012), there is a lack of studies that specifically examine abiotic controls regulating P form by fine sediment in gravel-bed streams.

River bed sediment is recognized as an important factor regulating soluble reactive P in the water column particularly during low flow periods (Jarvie et al., 2005). Deposited riverbed sediments influence P cycling by either binding or releasing P to overlying waters and have been recognized as legacy sources of P (Sharpley et al., 2013). To date, no studies have specifically examined the geochemical composition and particulate P forms of fine sediment within a gravel-bed river in a high-quality source water forested regions with multiple landscape disturbance

pressures. This research aims to quantify the geochemical controls influencing particulate P forms in suspended sediment and fine sediment in gravel-beds and evaluate the differential effects of sediment inputs from cumulative landscape disturbance pressures (roads, harvesting, wildfire, urban wastewater) on these abiotic controls. Specific objectives of the study are to:

1. Evaluate the spatial and temporal variability in the geochemical composition and particulate P forms of fine riverbed sediment in gravel beds of the Crowsnest River.
2. Compare geochemical and particulate P forms in riverbed fine sediment with suspended sediment with varying landscape disturbance in the Crowsnest River.
3. Examine abiotic controls governing particulate P forms in response to cumulative landscape disturbances.

2.3. Methods

2.3.1. Site Description

The Crowsnest River is a 5th order tributary of the Oldman River located in southwestern Alberta, Canada. This river drains a critical source water region on the eastern slopes of the Canadian Rocky Mountains. Elevation in the catchment ranges between 1100 m and 3100 m. Lodgepole pine (*Pinus contorta* var. *latifolia*) is the dominant vegetation cover at lower elevations (from Silins et al., 2014).

The underlying geology and surficial overburden of the basin is complex and diverse. The Crowsnest River drains several geological formations that include the Alberta Group, Belly River, Blairmore Group and Crowsnest (Langenberg et al., 2006). Precipitation to the watershed from July to September ranges from ~40 and ~65 mm. The average daily temperature for this period ranges from 9.5 and 14.3°C (Environment Canada, 2018a). In 2016, discharge measured at the Environment Canada 05AA008 gauging station of the Crowsnest River ranged from 1.7 and 4.8 m³s⁻¹ between July and September (Environment Canada, 2018b).

Study sites in the Crowsnest River were located downstream of tributary inputs from and reflect increasing downstream sediment pressures from a range of landscape disturbances that include historic and contemporary harvesting, wildfire, urbanization - sewage effluent. However due to historic impacts and differing degrees of roads, stream crossings and off-highway vehicle (OHV) use, differential effects of specific land disturbance types on PP form cannot be directly

evaluated. Study sites in the Crowsnest River are described in Table 2.1 and illustrated in Figure 2.1. Representative photographs of study sites are found in Appendix A.

Table 2.1. - Study site locations along the Crowsnest River.

Site ID	River	Category
S1	Below Crowsnest Lake	Most upstream site
S2	Below Allison Creek	Recreational tributary input (OHVs), historic harvesting, roads
S3	Below Star Creek	Harvested in 2015, roads, OHVs
S4A & B	Below Lyons Creek	Burned and salvage logged tributary input, roads, OHVs
S5	Below Frank Sewage Treatment Plant	Wastewater effluent
S6	Downstream Crowsnest River	~25 km downstream of S5 with additional sewage input, burned tributary input and small agricultural footprint

**Note: sites 2 to 4 have varying degrees of historic or contemporary harvesting, roads, road-stream crossings, or off highway vehicles use.

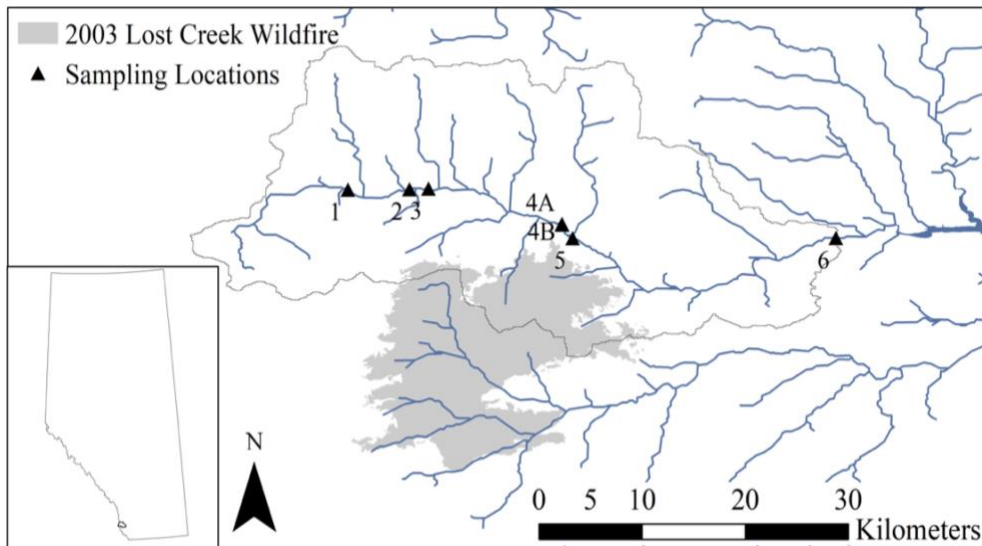


Figure 2.1. - Locations of study sites along the Crowsnest River.

2.3.2. Sampling Design

Fine surficial (10 cm) riverbed sediment deposited in gravel-beds was collected during low flow (July-September) in 2016 and 2017 using the method described by Lambert and Walling (1988). In the present study the term riverbed sediment will refer to fine sediment (<250 µm) stored within

the gravel-bed river. To provide representative samples of fine sediment at each site, a cylinder was randomly inserted into the gravel-bed matrix at several locations across each study reach. Fine sediment was re-suspended in the cylinder by disturbing the riverbed up to a depth of 10 cm with a plastic rod. A bilge pump was used to transfer the sediment-water mixture from the cylinder into a triple rinsed bucket. The sediment-water solution in each bucket was left undisturbed to settle for two days then the overlying water was decanted. The remaining slurry was placed into a zip-lock bag. A total of four composite samples were collected over a two-week period at each site between the 5th and 22nd August 2016. An additional three composite samples were collected at each site approximately every three weeks between July and August 2017 (19th July, 8th and 28th of August). All sediment samples were frozen and shipped to the University of Waterloo. The samples were later sieved and materials < 250 µm were retained for geochemical and P analyses.

Two time-integrated suspended sediment samplers (Phillips et al., 2000) were deployed at each study reach in the Crowsnest River from mid-July to mid-September 2016. The Phillips samplers were triple rinsed and installed horizontally at approximately 0.6 of the mean water depth (Phillips et al., 2000). Suspended sediment samples were collected by emptying the Phillips samplers into a triple rinsed bucket and left for two days for the fines to settle. Overlying water was siphoned off and the sediment slurry was placed into a ziplock bag, frozen and shipped to the University of Waterloo.

A freeze-core sampler, based on designs from Walkotten (1976) and Carling and Reader (1981), was used to collect a depth integrated sample of the gravel-bed matrix. The sampler was hammered into the gravel-bed to a depth of 30 cm, then compressed gas (R22a) passed through the cooling unit subsequently freezing gravel, sediment and interstitial water to the sampler. Sediment was removed from the sampler after the core began to thaw and then placed in a bucket. Riverbed bed samples were later placed in ziplock bags and shipped to the University of Waterloo for particle size analysis.

2.3.3. Laboratory Analyses

The physical characteristics, major element composition, and mineralogy of sediment were analyzed at a commercial laboratory (Act Labs, Burlington, ON) according to standard methods. Particle size distributions, median diameter (D_{50}) and specific surface area (SSA) were measured with a Malvern Mastersizer 2000. Major element composition (Si_2O , Al_2O_3 , CaO , MgO , Na_2O ,

K₂O, Fe₂O₃, MnO and P₂O₅) was determined by X-ray fluorescence and the results reported as percent dry weight (Mudroch, 1985). Analytical accuracy was confirmed using Canadian Reference Standards AGV-1, MRG-1, NCM-N, GSP-1, and SY-3 and comparing results with the stated reference values for major elements. Semi-quantitative mineralogy using the Rietveld method was determined using X-Ray Diffraction (XRD) and mineral diffraction patterns stored in International Centre for Diffraction Database (Activation Laboratories Ltd, 2018).

A sequential extraction scheme was used to fractionate particulate P into five operationally defined forms using the method described by Petterson et al., (1988). Non-apatite P (NAIP) which is considered the most bioavailable form is defined as the sum of three reactive phosphate fractions: loosely sorbed P (1.0 M NH₄Cl-P extractable P), reductant soluble P (0.11 M NaHCO₃.Na₂S₂O₄ extractable P), and metal oxide bound P (1.0 M NaOH extractable P) (Boström & Pettersson, 1982). Apatite P (AP) is the 0.5 M HCl extractable P fraction bound primarily to Ca and Mg carbonates and represents PP forms that are sensitive to low pH. This fraction is assumed to consist mainly of apatite P (natural and detrital), carbonate bound P, and traces of hydrolysable organic P. Thus, the AP fraction is considered a relatively stable, permanent sink of P in sediments (Kaiserli et al., 2002). The organic fraction (OP) is extracted using hot 1 M NaOH (85°C). Composite samples in 2016 were combined for each site and run in triplicate for QA/QC, see Appendix B.

2.3.4. Statistical Analyses

Kruskall-Wallis and Mann-Whitney rank sum tests were used to evaluate inter-site differences in particulate P form and physical sediment properties. A series of t-tests were used to examine differences in P forms (NAIP, AP, OP) and sediment type (riverbed and suspended). Student t-tests were performed for AP, OP and TPP as assumptions of equal variance were met (Levene's test). NAIP failed to meet assumptions of equal variance, therefore an adjusted Welsh t-test was used to assess differences between suspended and riverbed NAIP.

Particulate P forms and major elements were standardized (n=34), i.e., scaled data to a mean equal to zero and standard deviation equal to 1, for step-wise regressions in order to interpret the relative importance of parameters. A variance inflation factor (VIF, $1/(1 - R^2)$) was used to determine which variables would be distinct enough to avoid concerns of multicollinearity. The choice of a VIF threshold is ambiguous (Graham, 2003), however it has been argued that

multicollinearity is only severe if it is greater than 10 (Chatterjee et al., 2000). All variables (MnO, MgO, K₂O, Na₂O, organic carbon) fell below a threshold of five. Variables that were deemed sufficiently distinct were used in a stepwise regression to explore geochemical controls governing phosphorus binding to sediment.

Linear Discriminant Analysis (LDA) was used to explore which major element components best explain the site groupings. Additionally, LDA was employed to assess if any geochemical differences between sites could explain changes in PP form as a function of sediment geochemical composition. As a larger number of samples were run for major elements (n=49) than samples run for PP and organic carbon, VIF values were slightly different. Accordingly, this study used a VIF threshold of 5.5 in order to reduce concerns of multicollinearity while retaining the parameter LOI as other studies have demonstrated in the importance of organic carbon (LOI being a proxy of organic carbon) with PP forms (e.g., Mullholland et al., 1985). A confusion matrix for the LDA was calculated by removing a data point from each site and calculating the probability of being correctly classified.

Non-parametric Spearman's rank correlation coefficients were calculated between particulate phosphorus forms and major elements to compare results with those of previously reported studies. Spearman's rank correlation coefficients were used to explore relationships between major elements to aid in the interpretation of regressions with reduced parameters.

2.4. Results

2.4.1. Spatial variability in forms of particulate P in sediments

The distribution of PP forms for suspended and riverbed sediment are presented in Table 2.2 and Figure 2.2. Total particulate P concentrations (TPP) in riverbed sediment differed significantly among sites ($H(6) = 17.61, p = 0.007$). However, this was largely driven lower TPP concentrations at S1 and S4B in comparison to the other sites. Post-hoc analyses revealed statistically significant differences in riverbed TPP between S1 and all other sites ($p < 0.06$), with S1 having the lowest average TPP. Additionally, TPP concentrations at S4B were less than those at sites 2, 3, 4A and 5 ($p < 0.06$), and, site 6 was significantly less than site 2.

Table 2.2. – Spatial distribution of the mean (\pm standard deviation) of particulate P forms ($\mu\text{g/g}_{\text{sed}}$) in suspended (2016) and riverbed (2016, 2017) sediments from the Crowsnest River.

	Site	NAIP	AP	OP	TPP
Riverbed Sediments (n=4)	1	149.5 \pm 41.3	381.7 \pm 50.5	70.5 \pm 5.9	601.7 \pm 83.6
	2	104.4 \pm 23.0	546.0 \pm 27.3	58.1 \pm 8.4	708.6 \pm 26.8
	3	110.2 \pm 15.6	495.2 \pm 4.9	68.8 \pm 6.8	674.2 \pm 12.0
	4A	139.1 \pm 23.2	480.6 \pm 9.7	70.6 \pm 7.2	690.3 \pm 19.7
	4B	107.2 \pm 11.4	477.5 \pm 14.1	60.3 \pm 11.0	645.1 \pm 12.4
	5	150.1 \pm 31.6	471.7 \pm 7.2	60.8 \pm 6.3	682.7 \pm 31.7
	6	143.8 \pm 11.6	455.1 \pm 18.6	72.0 \pm 6.9	670.9 \pm 24.7
Suspended Sediments (2016; n=1)	1	248.9	277.0	79.5	605.4
	2	213.0	387.0	103.0	703.0
	3	191.2	355.0	102.0	648.2
	4	176.0	394.0	93.1	663.1
	5	314.7	392.0	102.0	808.7
	6	254.0	343.0	127.0	724.0

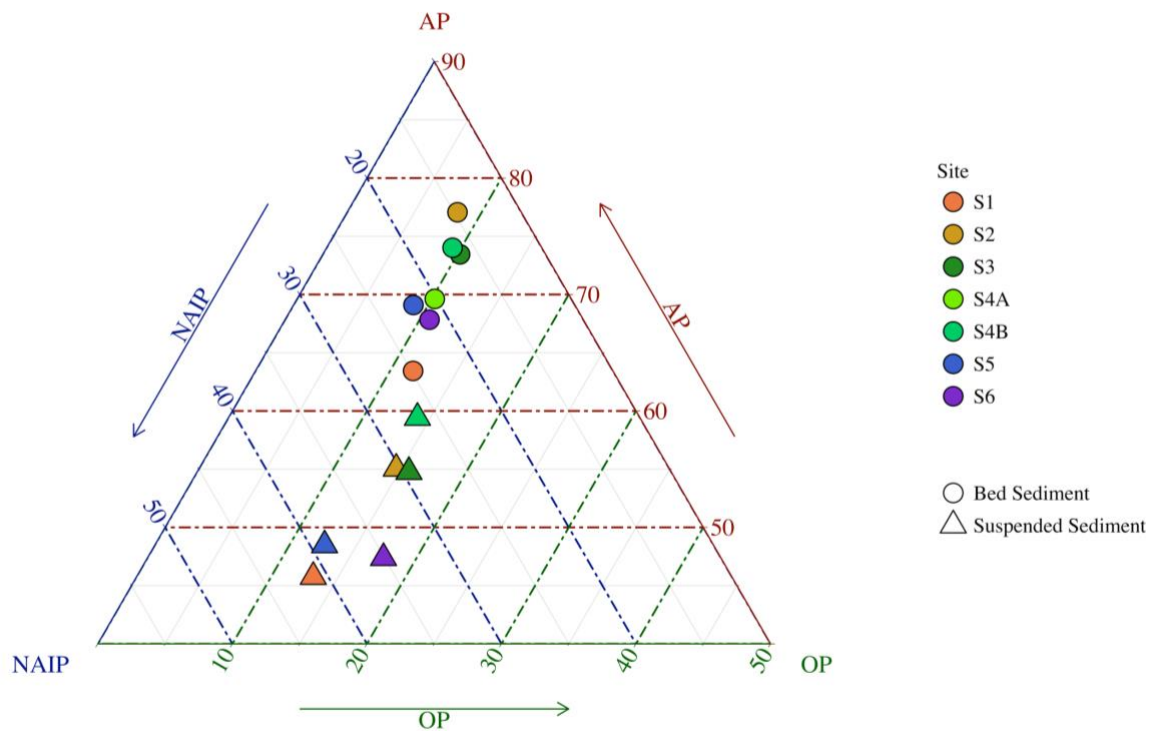


Figure 2.2. - Average particulate P form (%NAIP, AP, OP) in suspended and riverbed sediment.

The most bioavailable particulate P form (NAIP) in riverbed sediments varied considerably among sites ($H(6) = 12.48$, $p = 0.052$), but did not show a general spatial trend with distance from the most upstream site (S1) to the most downstream site (S6). For example, mean NAIP concentrations at S1 and S5 were similar (149.5 and 150.1 $\mu\text{g/g}_{\text{sed}}$, respectively). The only statistically significant differences for upstream sites 2 and 3 were with S6 ($p = 0.057$ and 0.029 respectively). Sites 4A and 5 came close to being statistically different ($p = 0.11$) to upstream sites (S2, S3). Apatite P was also significantly different across the sites ($H(6) = 23.03$, $p < 0.001$). Site 1 had significantly smaller concentrations of AP compared to all sites ($p < 0.05$), whereas site 2 had greater AP levels compared to all sites ($p < 0.05$). Site 3 had greater concentrations of AP compared to all sites except S2 ($p < 0.06$). OP was not significantly different among sites ($H(6) = 10.20$, $p = 0.117$), however the highest OP concentrations on average were at S1, S4A and S6.

Similar longitudinal patterns of PP forms expressed as a percentage of TPP were observed for suspended and riverbed sediments (Figure 2.2). TPP concentrations in suspended and riverbed sediment were relatively consistent ($t = 1.05$, $p = 0.300$; Table 2.2). However, AP represented a significantly smaller proportion ($t = -5.08$, $p < 0.001$) and NAIP was a greater component of TPP in suspended sediment ($t = 4.85$, $p = 0.003$). OP concentrations were also greater in suspended than riverbed sediment ($t = 7.74$, $p < 0.001$).

2.4.2. Geochemical properties of riverbed and suspended fine sediment

Major element composition and mineralogy

Inter- and intra-site variability in the geochemical composition of riverbed and suspended sediment in the Crowsnest River are illustrated in Figures 2.3 and 2.4, see Appendix A, tables A1 and A2 for average major element composition. Sediment at the most upstream site (S1) has a fundamentally different geochemical composition compared to other sites downstream in the Crowsnest River. At this site, the levels of MgO, CaO, LOI and OC were among the highest observed while other elements such as SiO₂, Fe₂O₃, Al₂O₃, MnO, Na₂O and K₂O were among the lowest. Riverbed geochemical data standardized by site (scaled data to a mean equal to zero and standard deviation equal to 1) are presented to highlight differences between major elements across sites (Figure 2.3). Notably, metal oxy-hydroxides (Al₂O₃, Fe₂O₃, MnO), Na₂O and K₂O content increased downstream and the three upstream sites were distinctly different from those downstream of S4.

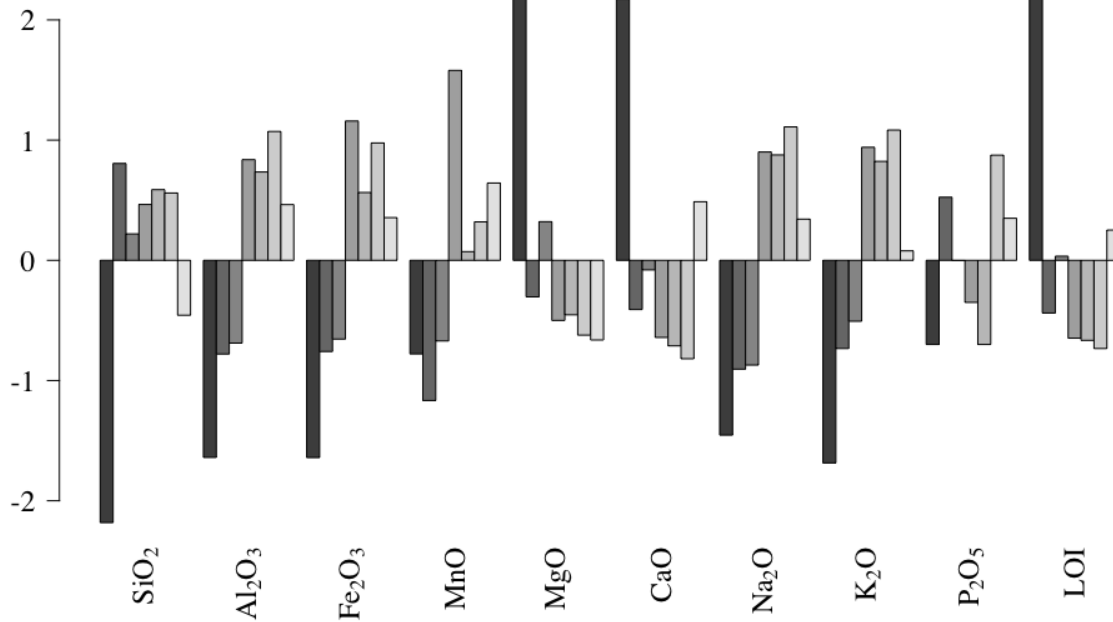


Figure 2.3. - Comparison of major element composition of riverbed sediments by site (n=7). Bar plot of standardized major element composition for each site (left to right represents upstream to downstream gradient).

Metal oxy-hydroxides and LOI content was higher in suspended than riverbed sediment ($p < 0.01$, Figure 2.4). Similar downstream trends of major elements were observed for suspended sediment. For example concentrations of Al_2O_3 , Fe_2O_3 and MnO were elevated at downstream sites (S4A-6). Concentrations of CaO and MgO were elevated in suspended sediment at sites 1 and 6 which may be attributed to geological controls linked to proximity of the Livingston and Belly River formations with the river and their influence on the geochemical control of local sediment sources. Finally, the highest LOI and organic carbon values were observed at S1 which may be attributed to an abundance of the *Didymosphenia geminata* mats observed at this site.

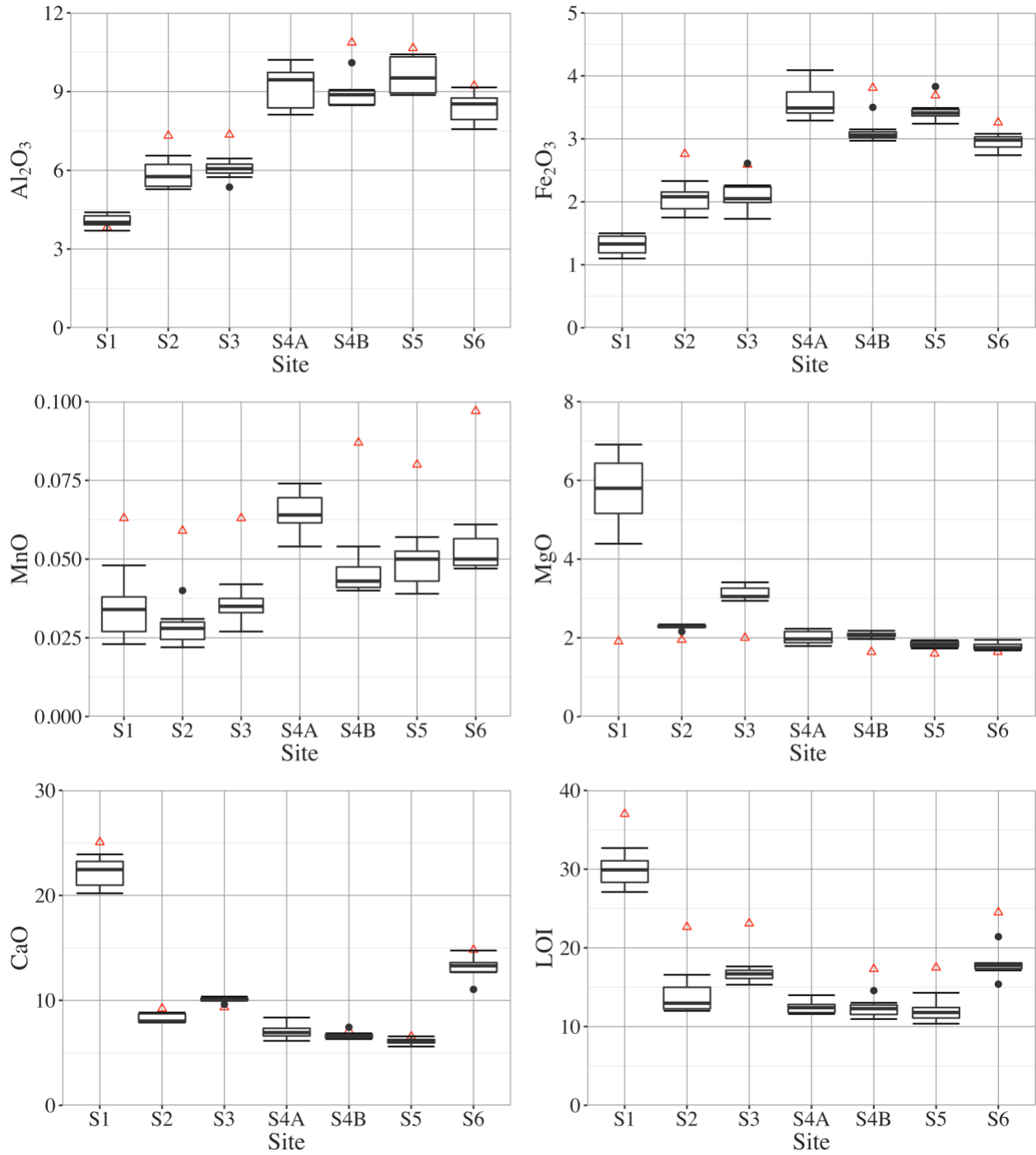


Figure 2.4. - Boxplots of deposited sediment (n=7 per site) with suspended sediment (n=1 per site) values represented by red triangles for different major elements (%) for 2016 (n=4 per site) and 2017 (n=3 per site).

The mineralogical composition of riverbed sediment is presented in Table 2.3. The data indicate that quartz, plagioclase, calcite and dolomite were the dominant minerals in the riverbed sediment but the percentages of muscovite, chlorite, kaolinite and K-feldspar were much lower. The mineralogy of S1 is remarkably different than the five other downstream sites - the percentages of calcite and dolomite were the highest amongst the study sites while quartz was the lowest. Levels of muscovite, kaolinite and chlorite were elevated at sites 4A-6 relative to sites 2 and 3.

Table 2.3. – Mineralogy of riverbed sediment at six study sites in the Crownest River in 2016 (% by mass of crystalline components)

Site	Quartz	Plagioclase	K feldspar	Muscovite	Kaolinite	Chlorite	Calcite	Dolomite
S1	27.3	1.7	1.2	4.6	1.1	nd	27.6	36.5
S2	65.4	4.6	2.6	6.4	1.2	nd	8.2	11.6
S3	51.2	4.6	nd	9.9	1.8	0.8	11.5	20.1
S4A	56.6	11.2	0.6	11	2.5	1.3	9.6	7.2
S4B	53.5	1.3	1	10.1	2.8	1.7	8.6	12
S5	52.4	12	0.6	10.4	2.7	2.2	10.5	9.2
S6	44.4	7.1	0.5	10.2	2.3	1.5	26.7	7.3

Physical properties of suspended and riverbed sediment

Particle size distributions of the gravel-bed materials are presented in Figure 2.5. The particle size distributions at Sites 1, 3 and 5 were similar, but site 5 had the smallest frequency of particles > 25 mm in the riverbed. In contrast, sites 2 and 6 had larger D₅₀ values, and therefore a greater frequency of larger cobbles. The composition of the riverbed sediment at sites 4B and 6 had particles that were larger than 50 mm, while all other sites consisted of smaller size fractions. The greatest difference between particle size distributions was between sites 4A and 4B, which were also distinct from other sites (Figure 2.5). Site 4A had smaller riverbed substrate with very fine and fine gravel, while site 4B had some of the largest cobbles. Across the study sites, the percent mass of fine sediment in the riverbed (<300 µm; Table 2.4) ranged from 2 to 8%.

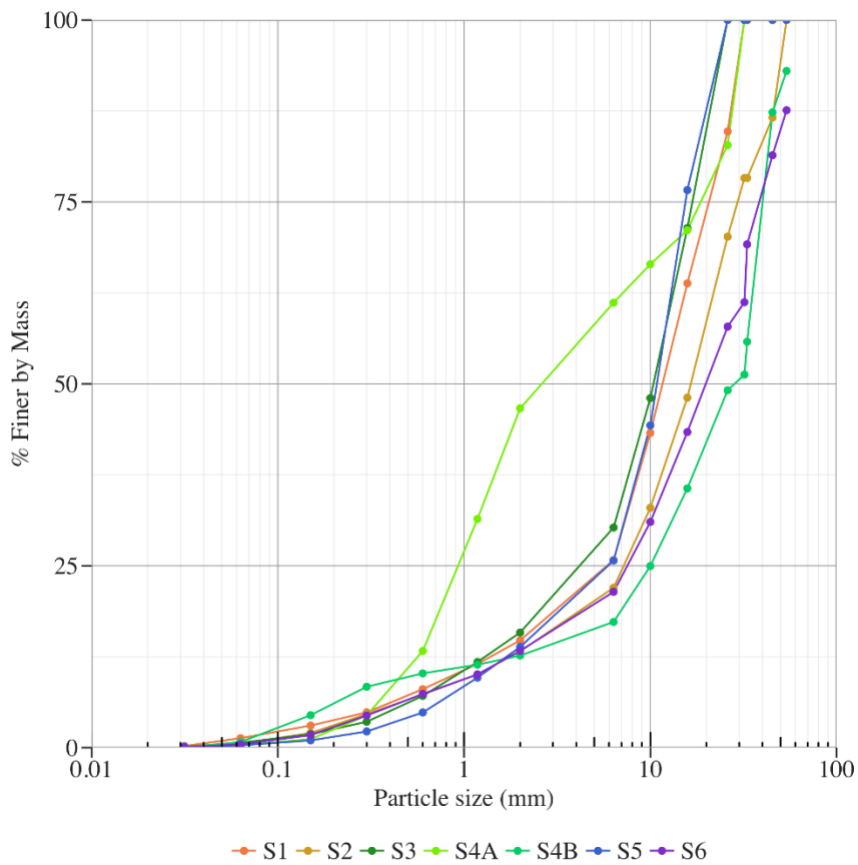


Figure 2.5. – Cumulative particle size distribution of the riverbed in the Crowsnest River

Table 2.4. - Particle size characteristics of riverbed substrate in the Crowsnest River

Site	D ₁₀ (mm)	D ₅₀ (mm)	% finer than 300 μm
1	27	11.7	4.9
2	47	17.5	4.6
3	23	10.3	3.6
4A	28	2.6	4.4
4B	49	27.5	8.4
5	21	10.9	2.2
6	54	19.9	4.4

Historically, fine cohesive sediment has been operationally defined as sediment < 63 μm (Wentworth, 1922). However, in the present study fine sediment is defined as materials (< 250 μm) because much of the fine sediment deposited on the gravel bed consists of soil aggregates and stable flocs that consist mostly of materials < 63 μm . The median particle size (D_{50}) for all samples were < 63 μm despite being sieved to a larger fraction. The mass of sediment < 300 μm accounted for less than 9 percent of the total weight of each sample (Table 2.4).

Cumulative particle size distributions of riverbed fine sediment (<250 μm) and suspended sediment are presented in Figure 2.6. Particle size distributions for riverbed sediment at all sites were similar ($H(6) = 3.3$, $p = 0.856$). Sites S1 and S3 had slightly lower D_{50} values than other sites, whereas S2 had the largest D_{50} (Table 2.5). The specific surface area of fine riverbed sediment ranged from 0.79 m^2g^{-1} (S2) to 1.06 m^2g^{-1} (S4B) but was not significantly different among sites ($H(7) = 2.2$, $p = 0.946$). Particle size distributions of suspended sediments were less variable across sites than riverbed sediment (Figure 2.6) and D_{50} values of suspended sediment were significantly smaller ($U = 158$, $p < 0.001$). The median particle size of suspended sediment ranged from 20.9 μm (S6) to 28.2 μm (S5). The specific surface area was significantly higher in suspended sediment ($U = 36$, $p\text{-value} = 0.029$) and ranged from 0.65 to 0.98 m^2g^{-1} at S5 and S6, respectively (Table 2.5).

Table 2.5. - Physical properties of fine river bed (2016, 2017) and suspended (2016) sediment

Site	Riverbed				Suspended			
	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	SSA (m^2g^{-1})	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	SSA (m^2g^{-1})
1	9 \pm 4	53 \pm 22	147 \pm 35	0.49 \pm 0.28	4.5	25.2	105.8	0.71
2	6 \pm 3	46 \pm 9	130 \pm 30	0.58 \pm 0.17	3.3	22.1	100.0	0.84
3	7 \pm 3	44 \pm 17	124 \pm 24	0.59 \pm 0.3	4.5	24.0	102.9	0.72
4A	6 \pm 3	41 \pm 8	130 \pm 48	0.63 \pm 0.24	-	-	-	-
4B	7 \pm 3	45 \pm 14	139 \pm 16	0.60 \pm 0.31	5.1	23.3	90.7	0.70
5	7 \pm 4	48 \pm 15	146 \pm 22	0.56 \pm 0.26	5.4	28.2	108.2	0.65
6	12 \pm 7	70 \pm 26	185 \pm 22	0.44 \pm 0.3	2.6	20.9	71.0	0.98

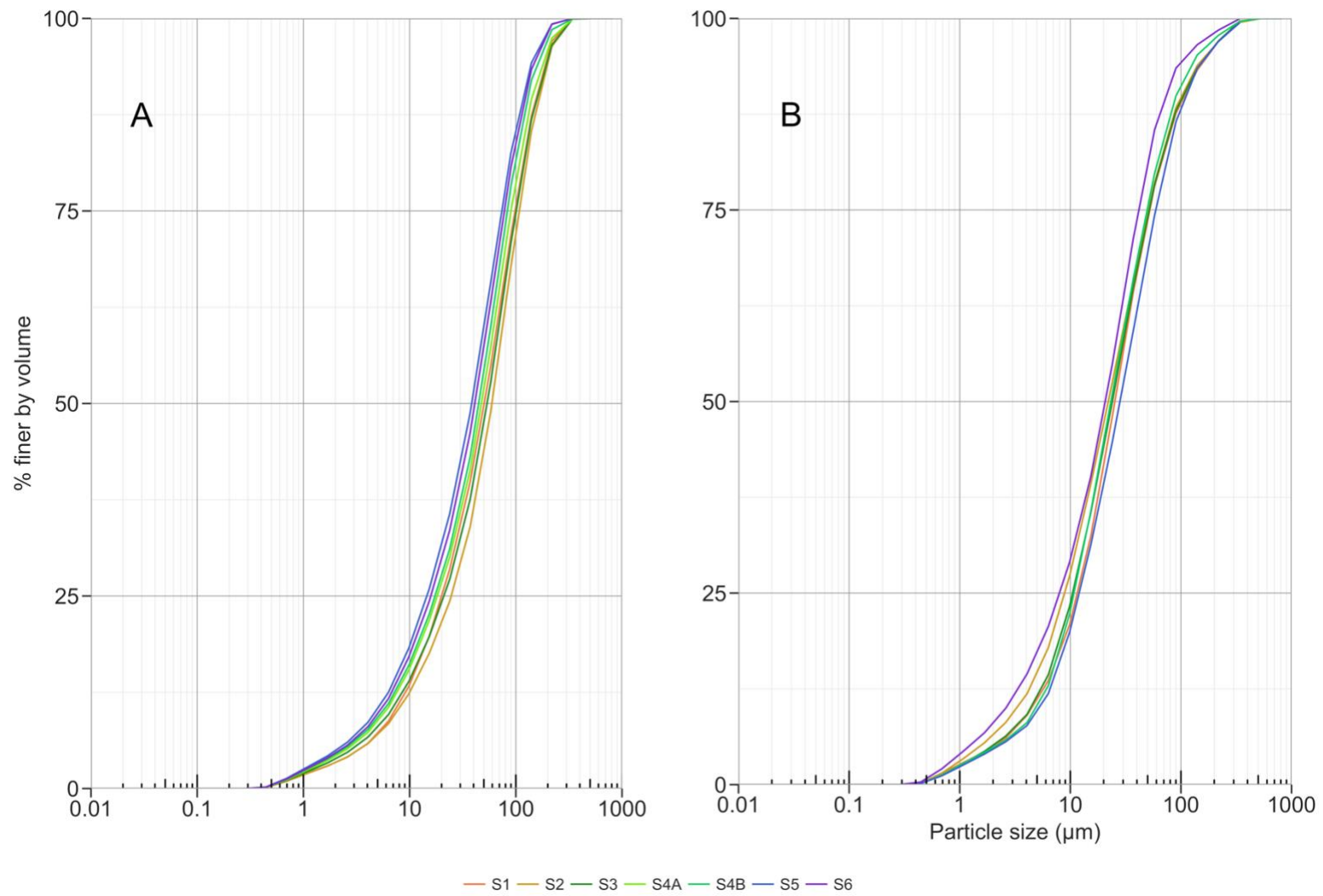


Figure 2.6. - Particle size distributions for fine sediment (<250 μm) for each sampling location in the Crowsnest River. Panel A represents average distributions for river bed sediment in 2016 and 2017 (n=4), Panel B depicts distributions for suspended sediment in 2016 (n=1).

2.5. Discussion

The form and concentration of PP in riverbed and suspended sediment can vary considerably in rivers globally (Figure 2.7). Total PP concentrations can range from <300 (i.e. McDowell & Sharpley 2003) to >6000 $\mu\text{g g}^{-1}$ (i.e. Owens & Walling 2002). The distribution and concentration of particulate P forms (NAIP, AP, OP) in fine riverbed and suspended sediment in the Crowsnest River are compared with data reported from other studies (Figure 2.7). The data show that the form and concentration of PP in the Crowsnest River suspended and fine riverbed sediment are comparable to some agricultural and urban impacted rivers but vary considerably between the water column, the riverbed, and across a single catchment. During low flow, the Crowsnest River remains relatively oligotrophic in comparison to other rivers for both suspended and riverbed materials. However, suspended sediment at S5 (below the sewage outfall) is comparable to mesotrophic systems, such as the Minnesota River (James & Larson, 2008) or the Maumee River (De Pinto et al., 1981; Figure 2.7). The Crowsnest River during low flow, appears to be shifting downstream of disturbances to levels of concern, exceeding Ontario Sediment Quality Guidelines of 600 $\mu\text{g g}^{-1}$ for lowest level effect (Persaud et al., 1993).

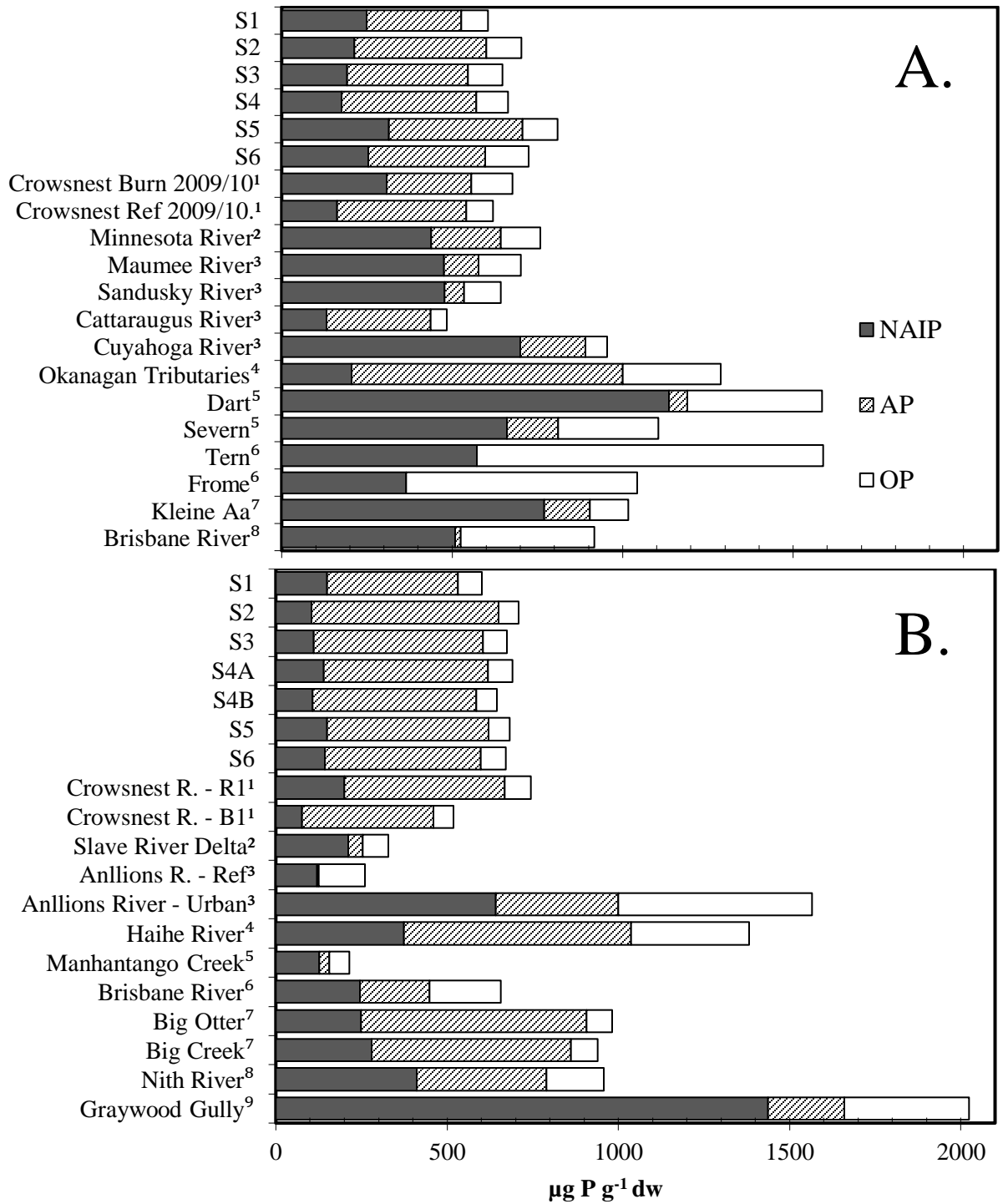


Figure 2.7. - Comparison of sediment-associated PP forms in the Crowsnest Rivers to those observed in agricultural and urbanized watersheds. Comparative plot of suspended (A) and riverbed sediments (B) from the literature. Ref A: 1. Allin, 2016; 2. James & Larson, 2008; 3. De Pinto et al., 1981; 4. Gray & Kirkland, 1986; 5. Walling et al., 2001; 6. Ballantine et al., 2008; 7. Pacini & Gachter, 1999; 8. Kerr et al., 2011. Ref B: 1. Allin, 2016; 2. Stone, 2004; 3. Barral et al., 2012; 4. Shujuan et al., 2009; 5. McDowell & Sharpley, 2003; 6. Kerr et al., 2011; 7. Stone & English, 1993; 8. Fogal et al., 1995; 9. Noll et al., 2009.

Spatial patterns of particulate P forms in fine riverbed and suspended sediment

Spatial and temporal variability in particulate P content and forms in riverbed and suspended sediment are related to differences in catchment characteristics, geology, hydro-climatic variability and landscape disturbances (Owens & Walling, 2002; Katsaouous et al., 2006). Despite sediment pressures from a range of disturbance types that impact the Crowsnest River, increases in TPP concentrations for fine riverbed and suspended sediment were largely attributed to the input of sewage effluent. The effect of primary sewage effluent on TPP and NAIP in fine riverbed sediment at site 5 in the Crowsnest River is shown in Figure 2.7 and these concentrations are comparable to previously reported data (e.g., Owens & Walling 2002; Jarvie et al, 2005; Barral et al., 2012). The largest average TPP concentration in riverbed sediments of the Crowsnest River was observed at S2 but this was primarily composed of AP (55%). The high percentage of quartz and feldspar in riverbed sediment has been attributed to the presence of larger particle size fractions derived from bank and allochthonous sources (e.g., Owens & Walling, 2002). While the differential impact of land-use cannot be parsed out, OHVs, road networks and historical harvesting impacts may be responsible for sediment erosion. Streambank collapse is common in this reach of the river during ice break-up which may be a missing link to the sediment P budget which is often unaccounted for (Fox et al., 2016). Increased TPP concentrations at 4A within the riverbed may be a result of legacy wildfire impacts, however these elevated concentrations were not reflected in larger substrate (S4B) and suspended sediment, the latter likely due to the ephemeral nature of the impacted tributary. Overall, confounding impacts of historic impacts from harvesting, roads and variable OHVs upstream of sewage inputs demonstrate large variability across this reach of the Crowsnest River. Suspended and riverbed sediment had high intra-site variability within and between years for TPP which can be related to macro-scale landscape processes, as well as with differences in PP forms and site-specific processes.

Particulate P forms are dynamic and are expected to change with different sediment sources (Owens & Walling, 2002) and environmental conditions such as pH and redox potential (Enell & Lofgren, 1988). The results of this study demonstrate the variability of PP forms of fine sediment within the gravel-bed across different tributary inputs, in particular NAIP changed across the catchment. Moreover, suspended sediment PP forms were highly variable across sites. NAIP is an important particulate P fraction as it is considered to be labile and bioavailable (De Pinto et al., 1981). In the Crowsnest River, NAIP in sediments was greater at sites impacted by sewage (S5,

S6), as well as sites 1 and 4A, see Table 2.2. Higher NAIP content and percentages at S1 can be partially attributed to PP loosely bound to Mg and Ca carbonates, which is removed from sediment in the NH₄Cl extraction (Reddy et al., 1999). This seems reasonable given that the mineralogical composition of sediment at this site consists principally of calcite and dolomite (Table 2.3). Furthermore, LOI was high at S1, suggesting that high NAIP at this site could be due to high organic matter which can promote flocculation (Stone & Droppo, 1994) and alter sediment properties (Stone et al., 2011). Extensive coverage of the diatom *Didymosphenia geminata* was noted at S1 during both summer (2016, 2017). Sundareshwar et al. (2011) examined the biogeochemistry of the stalks of *D. geminata* and concluded that they have an affinity for iron and P and that microbial processes can increase the availability of P. There were differences in NAIP at upstream sites (S2, S3) compared to S6 and with almost statistically significant differences with sites 4A and 5, demonstrating upstream to downstream differences in NAIP. NAIP varied considerably across sites, ranging between 10 to 40% of TPP. This highlights the dynamic nature of loosely-bound bioavailable forms of PP. The bioavailability of PP is related to sediment source type (Walling et al., 2008) and differences in aqueous chemistry (Withers & Jarvie, 2008). For instance, increased sewage typically increases aqueous P concentrations (Jarvie et al., 2006) which can sorb to sediments (Logan et al., 1982; Froelich, 1988) and this may explain elevated TPP and NAIP concentrations measured at sites 5 and 6. Similar to TPP at site 4, concentrations of NAIP were greater within the riverbed at S4A, but this pattern was not observed in suspended sediment at S4 or fine riverbed sediment at S4B. Furthermore, particulate apatite and organic P content changed as NAIP varied, suggesting modification of PP pools with environmental controls such as river morphology (Hendricks & White, 2000) and redox conditions (Golterman, 2004). This study found that over a reach and a stretch of river (~50 km), the PP forms, particularly NAIP, can change significantly with different disturbances during periods of low flow. Additionally, across a catchment differing sensitivities to landscape disturbance can be attributed to physical and biogeochemical processes influencing PP forms.

Contrasting suspended and riverbed sediments

Few studies have compared the differences of PP between riverbed and suspended sediments (e.g., House et al., 1995; Owens & Walling 2002; Su et al., 2014). Differences between suspended and fine riverbed sediment were significant for all PP forms in the fine sediment

fraction. House et al. (1995) showed that channel suspended and riverbed material behaved differently with regard to adsorption of P, where higher rates of uptake occurred with suspended material. In the Crowsnest River NAIP difference may be due to different sources of material, for instance a component of NAIP (NaOH-PP) has previously been attributed to top-soil erosion by Pacini and Gatcher (1999). Another explanation for the observed increase of NAIP in suspended sediment in the Crowsnest River is its interaction with dissolved P forms in the water column (Schlesinger, 2005). McCallister and Logan (1978) reported higher TPP concentrations in suspended sediments compared to deposited sediments. They attributed elevated P levels in suspended sediment to the binding of dissolved reactive P in the water column from point sources. General trends of increased AP and lower OP in riverbed sediments could reflect the ability of the river during low flow to transport larger particles, especially with smaller D_{50} values evident in suspended sediment. Kerr et al. (2011) attributed greater proportions of AP in riverbed sediment to particle sorting and selective transport of finer material in the Brisbane River, New Zealand. A previous study in the Crowsnest River reported that particulate P forms in suspended sediments varied seasonally, on PP forms in suspended sediment in 2009 and 2010 where average increases of 40 and 33% from spring to fall were measured (Allin, 2016). Therefore, the contrast in PP forms between suspended and riverbed sediment, particularly NAIP, could reflect seasonal transformations that have been observed in suspended sediment (Allin, 2016). Overall, contrasts in PP forms between suspended and riverbed sediments reflect differences in sediment source, changes in sediment water interactions and seasonal controls biogeochemical processes.

Hyporheic zones are considered important for biogeochemical cycling (e.g., Bardini et al., 2012), however there is limited information on how PP forms vary between riverbed and suspended sediments. The present study was conducted during low flow, where suspended sediment PP is most likely influenced by in stream biogeochemical processes rather than hydrological processes due to a limited active source area (e.g., Fogel et al., 1995), thus modified PP forms between riverbed and suspended sediments could reflect differing surface and subsurface processes. Assegid et al. (2015) showed that 70% of SRP variability could be explained by groundwater level, indicating that subsurface flow could play an important role in P cycling, particularly during low flow where groundwater fluxes are prominent (Soulsby et al., 1998). Therefore, groundwater controls could explain the reduced variability of fine riverbed sediment NAIP ($NAIP_{stddev}=29.4 \mu\text{g/g}_{sed}$) relative to suspended sediments ($NAIP_{stddev}= 50.5 \mu\text{g/g}_{sed}$) along

the main stem of the Crowsnest River. Previous studies have shown groundwater fluxes into bed sediments will alter the nutrient and carbon concentrations that ultimately influence the chemical and microbial processes (Mulholland et al., 1997; Bowes et al., 2003; Hauer et al., 2016). Coupling the flow and chemistry of the subsurface would progress our understanding of the drivers that bind P to particulate matter. The observed differences in PP forms between suspended and riverbed highlight the importance of the water column and hyporheic processes for the binding and transformation of P (Hendricks & White, 2000). Overall, suspended sediments were found to have higher biologically available forms of P than riverbed sediments at sites with active point source disturbances influencing the availability of P.

Physical and geochemical factors controlling particulate P forms

The bioavailability of particulate P in aquatic systems is governed by several physical and biogeochemical factors including redox conditions, temperature, particle size, sediment geochemistry, temperature and competitor ions (Stone & Murdoch 1989; Evans et al., 2004; Katsev et al., 2006, Su et al., 2014). Owens and Walling (2002) attributed differences in higher suspended TPP concentrations to grain size effects, where smaller particle sizes have increased levels of TPP and organic matter content. In the present study, suspended sediment had smaller particle sizes (D_{50}) relative to riverbed sediments ($t = -3.53$, $p = 0.0013$; Table 2.5), which could explain higher TPP concentrations in suspended material. Macro- and micro- morphological features can influence hyporheic interactions between the riverbed and surface water, impacting the transport of sediment and storage within the riverbed (Claret et al., 1997; Hendricks & White, 2000). The amount of subsurface flow and the degree of colmation due to the ingress and deposition of fine sediment in riverbeds can change with varying substrate size in rivers (Boano et al., 2014). In a study of PP forms in a gravel-bed river in France, Vervier et al. (2009) reported that hyporheic dynamics and grain size distributions were major controls on PP forms. In the Crowsnest River, S4A represented a straight channel section with a fine gravel/coarse sand riverbed, while substrate in S4B consisted of much larger cobbles and boulders, with faster flowing water due to channel constriction. The physical differences in substrate size and stream morphology between these two sites could help explain why differences in TPP ($p=0.029$) and bioavailable phosphorus ($p=0.057$) were observed between S4A and S4B. Although they were not directly measured, hyporheic processes, such as groundwater upwelling, were likely affected by

differences in grain size and the subsurface porosity which can alter subsurface flow rates. The physical properties (grain size) of riverbed fine sediment at these sites were similar, but there were significant differences between the grain size of suspended and riverbed sediment at these sites. Suspended sediment collected during periods of low flow will have a significantly smaller D_{50} and higher SSA than deposited fine sediment and therefore may influence the sorption and bioavailability of P in suspended sediments (Stone & English, 1993). In addition, elevated levels of organic carbon, LOI and MnO were observed in suspended sediments ($t=5.4, 2.5$ and 5.1 respectively, $p\text{-values}<0.05$). Accordingly, physical (particle size) and geochemical properties of the riverbed substrate and of the fine sediment influence how sediment is transported, stored in the riverbed, and how PP forms interact with the surrounding environment.

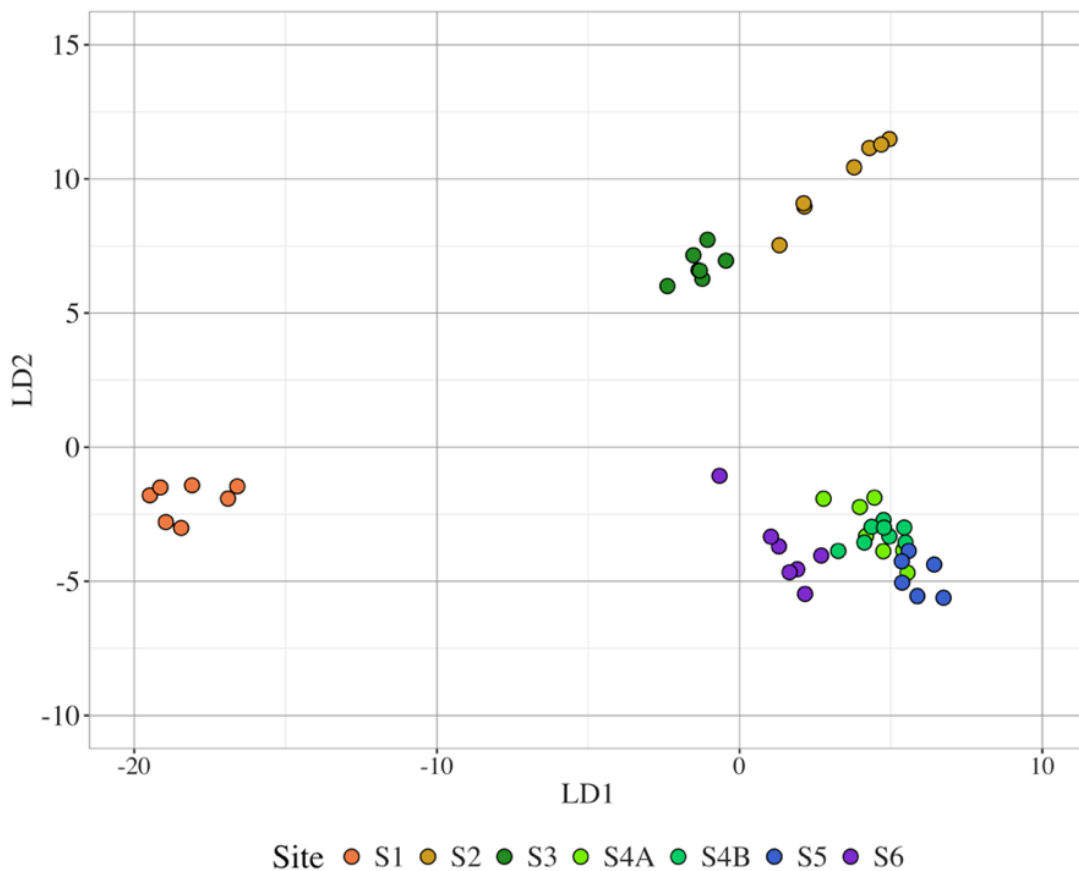


Figure 2.8. - First two components of LDA of deposited sediment, using geochemical variables that satisfied a VIF threshold to avoid issues of multicollinearity for 2016 and 2017.

Table 2.6. - Linear discriminant components for fine riverbed sediment, geochemical variables that satisfied a VIF < 6 to minimize issues of multicollinearity.

	LD1	LD2	LD3	LD4
MnO	-19.35	19.10	184.99	51.80
MgO	-2.91	-0.37	1.57	-1.24
Na ₂ O	0.26	-28.44	-6.54	-3.39
LOI	-0.70	-0.96	-0.43	0.20
Proportion of between site variation	0.657	0.320	0.017	0.006

Table 2.7. – LDA confusion matrix for prediction of classes

Actual	Predicted						
	S1	S2	S3	S4A	S4B	S5	S6
S1	1.00						
S2		0.86	0.14				
S3			1.00				
S4A				1.00			
S4B					0.86		0.14
S5					0.29	0.71	
S6							1.00

The geochemical composition of sediments influence how P will bind and PP availability (Stone & English 1993; van der Perk et al., 2006), thus differences in sediment geochemical properties can provide insight into P processes. Several differences in the major element composition (metal oxides) were observed for fine riverbed and suspended sediment at sites along an upstream-downstream gradient in the Crowsnest River. Site differences in the percent CaO and MgO may reflect the effect of surficial geology on sediment source along the entire study reach. Interestingly, the Crowsnest River flows nearly diagonally across several geological formations and the input of sediment from these distinct geological sources is likely an important factor responsible for the observed geochemical composition of sediment at each study site. In contrast, differences in LOI and OC could be due to different biological feedbacks with different nutrient dynamics and availabilities (Borch et al., 2010; Battin et al., 2016). The content of calcite and dolomite in sediment ranged between 17% and 64% in the Crowsnest River. Higher percentages of calcite and dolomite were measured at S1 and S6 likely due to the unique parent geology above these sites. Accordingly, precipitation of P with calcium may play an important role in P availability (e.g., House & Denison, 2002) however, further investigation of this hypothesis is required.

Differences in the major element composition between sites were determined with linear discriminant analysis (see Table 2.6, 2.7, and Figure 2.8). The results of this analysis show that most of the variance between sites was captured by MnO and Na₂O. The latter two variables are correlated with other oxy-hydroxides, e.g., Fe₂O₃ and Al₂O₃ (see Table 2.8). The distinctions between sites 2, 3 and 4-6 with regard to metal oxy-hydroxides allowed for sites to be separated (Figure 2.8), suggesting that metal oxy-hydroxides are strongly influencing PP forms between upstream and downstream sites. Other studies report the importance of sediment geochemistry and redox-sensitive metal oxy-hydroxides in governing both the form and mobility of PP forms in rivers (Uusitalo et al., 2003; Ellison & Brett, 2006; Aguedulo et al., 2011). Distinct differences in NAIP were observed between S4A and B despite being geochemically very similar, which suggests environmental controls are creating the distinct between these sites. Separation of site 1 can be attributed to much higher LOI values relative to other sites, which suggests that organic carbon processes are driving chemical differences (Borch et al., 2010). Distinct geochemical differences between upstream sites 2-3 and downstream sites 4-6 were observed (Figure 2.4) may be due to sediment sources, geology and environmental conditions of the riverbed (Brunke & Gosner 1995; House, 2003), which could reflect differences in PP forms. While geochemistry provided insight into the complex nature of PP forms, it is apparent that responses to landscape will differ given biogeochemical properties of the aqueous environment.

Table 2.8. - Spearman Rank Correlation coefficients for suspended and riverbed sediments (n=34) from the Crowsnest Watershed 2016-2017

	NAIP	AP	OP	TPP
SiO ₂	-0.63	0.77**	-0.68**	0.29*
Al ₂ O ₃				
Fe ₂ O ₃				0.32
MnO	0.76**	-0.51**	0.47**	
MgO	-0.50**	0.39*	-0.30	
CaO		-0.35*	0.29	
Na ₂ O		0.33	-0.43*	
K ₂ O				
LOI	0.52**	-0.62**	0.55**	
OC	0.61**	-0.59**	0.66**	
D50			-0.42*	
SSA			0.35*	

Unmarked p < 0.1, * p < 0.05, **p < 0.01

Major elemental composition of sediment has been shown to correlate with different forms of PP (Stone & English, 1993; Lopez et al., 1996) and results of the present study show that major element composition can help to predict different forms and availability of PP in Crowsnest River sediment. A step-wise regression approach was used to determine whether geochemical properties of the sediment could be used to predict NAIP in the Crowsnest River (Table 2.9). The results show that MnO and organic carbon can be used to model NAIP content in the Crowsnest River (R^2_{adj} : 0.753, $p < 0.01$). The role of organic matter and metal oxy-hydroxides in the form and mobility of P in aquatic systems has previously been described (Stone & English 1993; House et al., 1999; Evans et al., 2004) and the results of the present research are consistent with earlier work. The largest outlier for NAIP was a suspended sediment sample at S5, below the sewage outfall where one of the lower organic carbon and LOI values were observed. Organic matter contributes to the adsorption of phosphorus (McDowell et al., 2001; House & Denison 2002) and previous work in this watershed has shown relationships between OC and NAIP (Emelko et al., 2016). Microbial activity is a function of available substrate and organic matter content (Boulton et al., 1998; Findlay, 2010). Therefore limited available organic matter in the Crowsnest River may limit microbial release of phosphorus (Golterman, 2004; Kronvang, 1992). Interactions of major element composition with AP and OP demonstrated in stepwise regression models highlight the complex nature of particulate P binding and availability. The presence of interactions in both models indicates that geochemical components change the relationship of P forms based on what major elements are present, additionally the magnitudes of these interactions are likely to change with different hydrological conditions. Overall, NAIP varied as a function of OC and MnO, suggesting that across the Crowsnest River PP availability was driven by electron donor availability and P bound to metal oxides, while AP and OP forms are not just based on one major element, but how major elements interact with each other and P.

Table 2.9. – Step-wise multiple regressions for standardized particulate P form (n=34) using standardized major element data

Predictor variable	Formula	R ² _{adj}	p-value
NAIP	$1.13 \cdot 10^{-16} + 0.45 \cdot \text{MnO} + 0.63 \cdot \text{OC} + 0.22 \cdot \text{K}_2\text{O}$	0.762	$4.4 \cdot 10^{-10}$
AP	$0.47 - 0.58 \cdot \text{OC} - 0.20 \cdot \text{MnO} + 0.71 \cdot \text{MgO} - 0.17 \cdot \text{Na}_2\text{O} + 1.20 \cdot \text{MgO}:\text{Na}_2\text{O} + 0.38 \cdot \text{MnO}:\text{Na}_2\text{O} + 0.47 \cdot \text{OC}:\text{MgO}$	0.942	$8.37 \cdot 10^{-16}$
OP	$0.05 + 0.46 \cdot \text{MnO} - 0.84 \cdot \text{Na}_2\text{O} + 0.53 \cdot \text{K}_2\text{O} - 0.26 \cdot \text{MnO}:\text{Na}_2\text{O}$	0.814	$4.82 \cdot 10^{-9}$
TPP	$7.6 \cdot 10^{-16} - 0.56 \cdot \text{MgO}$	0.289	$6.24 \cdot 10^{-4}$

Implications of landscape disturbance of PP forms

The present study was conducted to examine the cumulative effects of sediment pressures from various disturbance types on the form of PP in the Crowsnest River, Alberta. Results of the study demonstrate the dynamic nature of PP forms in fine riverbed and suspended sediment across different landscape disturbances. In this study, redox-sensitive components, i.e., metal oxyhydroxides, were strongly associated with the most bioavailable particulate P form (NAIP) and disturbance. However, PP forms and sediment geochemistry were variable within and between sites, suggesting that micro-scale processes could be important for accurately depicting P cycling in rivers. Future research should couple particulate and aqueous chemistry to better understand the abiotic drivers of changes in major elemental composition and therefore the ability of sediment to bind and release P.

Assessing landscape disturbances in the context of cumulative effects can be difficult due to the multifaceted nature of landscape disturbance and hydro-climatic variability on PP source, transport, form and availability. In order to approach water quality management in a more holistic way there is a need for extensive sampling to capture the variability within the system, as point sampling of PP forms can over or underestimate the risk to eutrophication. In the present study, differences in PP forms between fine riverbed and suspended sediment were observed, which may be a product of different surface and subsurface processes. Furthermore, riverbed PP forms varied considerably over a reach suggesting the importance of hotspots and “micro-niches” (Stockdale et al., 2009). Despite being highly variable, sites downstream of sewage inputs demonstrate the significant impact of point sources for P availability. In the Crowsnest River PP availability was greater in very fine to fine gravel substrate, but not in coarse gravel substrate, illustrating the differences in sensitivity within a river reach due substrate heterogeneity and morphology. Spatial

patterns of PP were complex and varying degrees of landscape disturbance were apparent with the heterogeneous nature of both micro- and macro- features of the river.

2.6. Conclusion

The present study was conducted to evaluate the abiotic control of fine sediment on phosphorus form in gravel bed streams. The spatial distribution of major elements and particulate phosphorus (PP) forms (NAIP, AP, OP) in riverbed and suspended fine sediments (<250 μm) were determined to examine the effect of landscape disturbances on PP form and bioavailability during environmentally sensitive conditions of low flow in the Crowsnest River, Alberta. Conclusions of the study are:

1. Landscape disturbances influenced PP bioavailability with differing degrees of sensitivity.
2. Point sources inputs of P (sewage effluent) had the greatest influence on suspended sediment PP content and availability.
3. NAIP in fine riverbed sediment constituted 11-30% of TPP, while suspended sediment NAIP accounted for almost double the proportion of TPP (27-41%).
4. Based on an analysis of metal oxide and organic matter content as well as particle size distribution and specific surface area, suspended and fine riverbed sediment represent two distinct populations of sediment in the Crowsnest River.
5. Differences between suspended and riverbed sediment are likely due to different sources, biota and differences in surface and groundwater controls.
6. Redox-sensitive metal oxides and organic carbon largely explained the spatial variation in NAIP forms.
7. Retention of sediments and heterogeneous morphological responses to PP forms highlights the difficulty in assessing landscape disturbances and cumulative effects.
8. Overlapping landscape disturbances in space and time, as well as varying degrees of disturbance produce variable responses to PP availability. Therefore, uncertainty of sediment source apportionment means impacts cannot be differentially assessed.

Chapter 3

Fine sediment phosphorus mobility in a gravel-bed river

3.1. Summary

Landscape disturbance pressures in forested headwater regions can modify both the supply and transport of sediment from hillslopes to river networks. The effects of these pressures on phosphorus (P) mobility in rivers vary regionally depending upon the type and severity of the disturbance as well as interactions amongst other watershed scale controls such as climate, geology, hydrology and vegetation. The present study examines P dynamics in a gravel-bed river across multiple disturbances during environmentally sensitive periods of summer low-flow. Six study sites were selected to represent a gradient of sediment pressures from landscape disturbances (e.g., roads, harvesting, wildfire, sewage) in the Crowsnest River, Alberta. Interactions between fine bed sediments and soluble reactive phosphorus (SRP) were examined using equilibrium phosphorus concentrations (EPC_0) and diffusive fluxes of SRP from the riverbed sediments. Diffusive fluxes at each site were estimated using gradients of SRP between pore-water in the bed and water column, determined from vertical distributions of SRP in the gravel matrix measured with pore-water peepers. SRP concentrations in pore-water were variable among depths and sites but were elevated downstream of the stream reach receiving primary sewage effluent outflow. Larger SRP concentration gradients were observed at sites that had either smaller substrate or increased biofilm activity. The EPC_0 and diffusive pore-water flux data suggest that fine sediment in the riverbed acted as a source of SRP to the water column under low-flow conditions, when the risk for eutrophication is higher and such conditions favor the growth of biofilms. EPC_0 concentrations showed large inter- and intra-site variability indicating heterogeneous responses to disturbance. Furthermore, overlapping and varying proportions of historic and contemporary harvesting, roads, road-stream or culvert crossings, and OHV use confounds the apportionment of landscape impacts. This study provides insight into the potential for the regulation of P by sediments in gravel-bed rivers following a range of landscape disturbance effects.

Key words: Fine sediment; channel bed sediment; equilibrium phosphorus concentration; sorption; gravel-bed rivers; pore-water phosphorus

3.2. Introduction

In North America, source waters for the majority of drinking water supplies originate in forested landscapes (Jones et al., 2009). Accordingly, both natural and anthropogenic large-scale landscape disturbances in these critical source water regions can strongly influence both quality and quantity of surface waters (Bladon et al., 2014). Several studies have shown that the mobilization and transfer of sediment and associated nutrients from hillslopes to rivers is strongly increased by wildfire (Wondzell & King, 2003; Kunze & Stednick, 2006; Westerling et al., 2016; Emelko et al., 2016). Likewise, harvesting can increase sediment delivery to streams, which can affect water quality through the transport and storage of fine sediments and associated nutrients in riverbeds (Binkley & Brown, 1993). Urban landscapes can significantly alter sediment and P dynamics in rivers (House & Denison, 1997; Haggard et al., 2005) and sewage effluent without proper treatment can be detrimental to the water quality of aquatic systems (Jarvie et al., 2006). Furthermore, impacts that increase runoff that accelerates erosion and mobilize sediment from the landscape can have long-lasting effects on water quality (Ellison & Brett, 2006). The deposition of nutrient enriched sediment from upstream sources on riverbeds can act as sources of sediment and associated nutrients that create lag-time effects in ecosystem recovery after a disturbance (Meals et al., 2010).

Phosphorus (P) is the limiting nutrient in freshwater environments and soluble-reactive P (SRP) is considered the most bioavailable form of P (Schindler, 1977; Correll et al., 1998). Fine sediment ($< 63 \mu\text{m}$) is the primary vector for P transport in river systems (Ongley et al., 1992; Owens et al., 2005) and it can play an important role in the retention and release of P within a river reach (Stone & Mudroch, 1989; House, 2003). Moreover, fine sediment within a riverbed can adsorb and desorb SRP to the water column and transform forms of P through different biogeochemical processes (Reddy et al., 1997; Bowes et al., 2003; Jarvie et al., 2005). Riverbeds have been identified as important sources of sediment and SRP during low flow conditions in impacted systems (Jarvie et al., 2005; Ballantine et al., 2006) but few studies have rigorously addressed this issue- particularly, during low flow where residence times of surface water in the riverbed are high, and, this longer contact time increases the potential for the buffering of SRP from the water column during this time (Jarvie et al., 2005). Accordingly, a better understanding of the role of riverbeds as either sources or sinks of P is needed for proper watershed management

and for assessing impacts to aquatic ecology (Lottig & Stanley, 2007; Stutter & Lumsdon, 2008; Withers & Jarvie, 2008).

The storage of fine sediment in riverbeds can influence the fate of particulate P (PP) in streams (Reddy et al., 1999). The physical and geochemical properties of sediment can affect the rates and magnitude of P sorption to riverbed sediment (Froelich, 1988; Evans et al., 2004; Lottig & Stanley, 2007). Differences in the physical and chemical composition of riverbed material can vary with historical land-use, which can produce a diverse set of ecological responses (Sharpley et al., 2014). Mineral composition (such as the presence of iron oxides) is a major control on the adsorption/desorption process, but is strongly influenced by changing redox conditions (Stone & Mudroch, 1989; Neal, 2001; House & Denison, 2002; Golterman, 2004). Phosphorus sorption in surface waters is increasingly being studied in an attempt to characterise catchments and their impacts on water quality (Stutter & Lumsdon, 2008; McDowell, 2015; Emelko et al., 2016). Previous research on riverbed sediment and P interactions has been primarily conducted in rivers impacted by agricultural and urban land use (e.g., Vallet et al., 1990; Mulholland et al., 1997; Vervier et al., 2009). Although the storage and fate of fine grained and P enriched materials in coarse gravel-bed rivers have recently been shown to influence the abiotic control of PP in the water column of many New Zealand rivers (McDowell, 2015), no studies have been conducted to examine the effect of land disturbance impacts on fine sediment in riverbeds and their impact on P mobility in gravel bed rivers on the eastern slopes of the Rocky Mountains under different landscape disturbances in forested watersheds.

In this study, the P-exchange characteristics of bed sediments are examined in the Crowsnest River along a downstream gradient of increasing sediment pressures resulting from varying land-use during low flow conditions. Measurements of the Equilibrium Phosphorus Concentration, EPC_0 (Taylor & Kunishi, 1971; Stone & Mudroch, 1989; Jarvie et al., 2005; Emelko et al., 2016) were conducted to determine the extent to which riverbed sediments act as a source or sink of SRP to/from the overlying water column. Accordingly, the primary goal of this research is to examine the abiotic control of fine sediment on P dynamics in a gravel-bed river in a critical source water region on the eastern slopes of the Rocky Mountains in Alberta, Canada. The specific objectives of the study are to:

1. Evaluate the vertical distribution of SRP in gravel beds and overlying waters and calculate SRP fluxes from the riverbed along a downstream gradient of the Crowsnest River;
2. Examine the P sorption characteristics (EPC₀, y-intercept (α) interpreted from sorption isotherms) of fine sediment (<250 μm) in reaches of a gravel-bed river with different landscape disturbances; and,
3. Characterize associations between P dynamics, environmental conditions (dissolved oxygen and temperature) and the physical properties of the bed.

3.3. Methods

3.3.1. Site Description

The Crowsnest River is a tributary of the Oldman River located on the eastern slopes of the Rocky Mountains in southwestern Alberta (Figure 3.1). Several natural (wildfire) and anthropogenic (roads, UHVs, harvesting, urbanization – sewage inputs) landscape disturbances have occurred in this critical forested source water region (Emelko et al., 2010). The cumulative effects of these sediment disturbance pressures on fine sediment-associated P mobility in gravel bed rivers and the processes that propagate these materials downstream are not well documented.

Elevation in the Crowsnest watershed ranges from 1100 to 3100 m above sea level. Vegetation across these elevation differences includes mixed conifers, subalpine and alpine meadow (Ho, 2013). Lodgepole pine (*Pinus contorta* var. *latifolia*) is the dominant forest cover at lower elevations, whereas Engelmann spruce (*Picea engelmannii*) and subalpine fir (*Abies lasiocarpa*) are dominant at higher elevations (Emelko et al., 2016). The underlying geology in the watershed consists primarily of Cretaceous shales, limestones, dolomite and sandstone, overlain by well to imperfectly drained Brunisols (Eutric and Dystric) soils (Bladon et al., 2008). Surficial materials in the basin consist of complex glacial-fluvial deposits that consist of materials ranging in size from clay to gravel (Langenberg et al., 2006).

Mean annual precipitation in the study area ranges from 700 and 1700 mm yr⁻¹ and ~55% of the precipitation occurs as rain during the frost free period (Emelko et al., 2016). The mean annual temperature is 4.6 °C which fluctuates seasonally from -7°C (January) to 16°C (July) (Emelko et al., 2016). Between 1965 and 2013, the average discharge of the Crowsnest River at the Frank gauging station (WSC 05AA008) was $4.67 \pm 4.37 \text{ m}^3 \text{ s}^{-1}$.

A range of large scale natural and anthropogenic landscape disturbances have occurred in the Crowsnest River basin. The 2003 Lost Creek wildfire burned a nearly contiguous area of 21,000 ha that continues to affect water quality of Crowsnest River more than 6 years postfire (Emelko et al., 2016). In 2014, a tributary to the Crowsnest River (Star Creek) was harvested using 3 different harvesting techniques (clear cut, variable retention and strip cut). Other disturbances such as historical harvesting, roads, UHV use, stream crossing, urbanization, a golf course and sewage treatment plant effluent in the basin exert increasing downstream sediment pressures in the Crowsnest River. The largest withdrawal of water from the river is for commercial purposes; predominantly for the Allison Creek Fish Brood Station and Hatchery (Oldman Watershed Council, 2010).

The six study sites are located along a 55 km reach of the Crowsnest River (Figure 3.1, Table 3.1). To minimize morphological differences between sites instruments were deployed in riffles at the downstream end of pools. The least impacted site by land disturbance (reference site - S1) is located immediately below Crowsnest Lake. Site S2 is located above the confluence of Star Creek with the Crowsnest River and this site receives tributary inflow from a sub-catchment that has an extensive ATV trail network. Site (S3) is located below a harvested watershed (Star Creek) site S4 receives tributary input from a watershed impacted by the 2003 Lost Creek wildfire and post fire salvage logging. The river morphology at Site 4 did not have a well-defined pool and riffle sequence so two sites were selected at S4: the grain size of river substrate at S4A was finer (fine gravel), while bed materials at S4B were dominated by cobbles. Sites two to four represent tributary inputs that all have varying proportions of historic or contemporary harvesting, roads, road-stream or culvert crossings, and OHV use, therefore discerning individual effects of landscape disturbances on P mobility is not possible at these sites. Site S5 is located below the sewage treatment plant effluent and was monitored to observe point source impacts on riverbed P dynamics. Site S6 was located ~25 km downstream from S5 and had additional inputs from sewage from the town of Hillcrest located approximately ~20 km upstream, Drum Creek which was burned during the 2003 Lost Creek wildfire and was the only site to have a small agricultural footprint. Similar to site 4, site 6 did not have a typical pool-riffle sequence but had a wide channel (~ 30 m) and was shallower than all other sites.

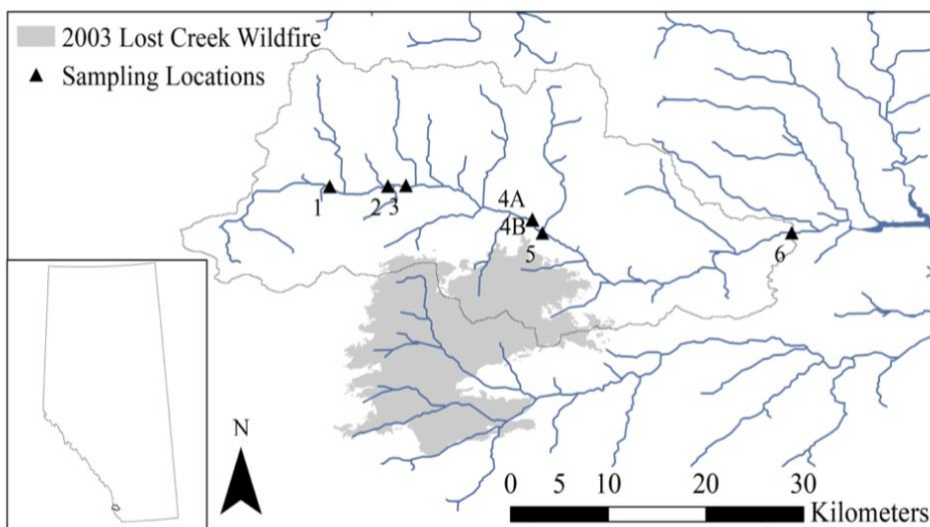


Figure 3.1. - Study site locations along the Crowsnest River.

Table 3.1. - Study site locations (upstream to downstream) along the Crowsnest River.

Site ID	River	Category
S1	Below Crowsnest Lake	Most upstream site
S2	Below Allison Creek	Recreational tributary input (UHVs), roads, historical harvesting
S3	Below Star Creek	Harvested in 2015, roads, UHVs
S4A & B	Below Lyons Creek	Burned and salvage logged tributary input, roads, UHVs
S5	Below Frank Sewage Treatment Plant	Wastewater effluent
S6	Downstream Crowsnest River	~25 km downstream of S5 with additional sewage input, burned tributary input and small agricultural footprint

**Note sites 2 to 4 have varying degrees of historic or contemporary harvesting, roads, road-stream crossings, or off highway vehicles use.

3.3.2. Field Equipment and Sampling Design

The study was conducted over an eight-week period in 2016 (August and September) and additional surficial sediment was collected in 2017 over an 9-week period (July and August). A field program was developed to sample pore-water and surface water, surficial fine-grained sediment and fine sediment infiltrated in the gravel-bed matrix as well as environmental parameters (temperature and dissolved oxygen). Three pore-water peepers (PWP) (Hesslein, 1976) were installed at each study site to sample pore-water and surface water to determine SRP fluxes from the sediment. The PWP were 40 cm long and 12 cm wide; each having 26 sampling

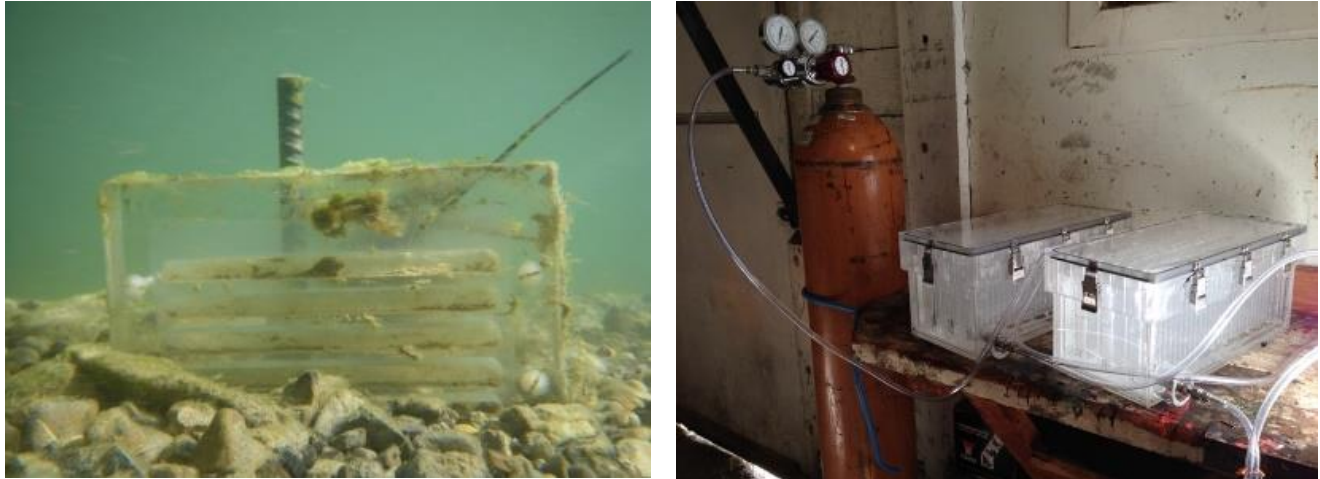


Figure 3.2. - Left – Porewater peeper installed in gravelbed; Right – Pore-water peepers in environmental chambers while being purged with N₂

cells with a volume of 4 cm³ cell⁻¹ (Figure 3.2). The pore-water peepers were washed with Extran to remove any potential debris from manufacturing or previous use. The samplers were soaked in 20% H₂SO₄ for 24 hours then triple rinsed using Milli-Q water. The PWP's were assembled in a deionized (DI) water bath by placing a 0.45 µm Nytex screen placed on top of the PWP after which the front panel was fastened to the back panel. Before deployment, PWP's were placed in Plexiglass environmental chambers (Figure 3.2) and purged with N₂ gas to remove oxygen. PWP's were deployed between August 3rd and 5th 2016 and removed between September 29th and October 5th 2016. Immediately after removing the PWP's, a syringe was used to collect water from each cell and immediately filtered (0.45 µm cellulose acetate filters). PWP's were sampled from the bottom to the top to minimize potential influences of anoxia. Water samples from PWP's were stored at 4 °C and shipped to the University of Waterloo for analysis.

Depth integrated water column samples were collected every other day in August 2016 (n=12), with less frequent sampling in September 2016 (n=3 to 5, varied by site). At each collection period and site, two water column samples were collected in acid-washed (20% HCl) triple-rinsed high-density polyethylene bottles and kept at 4 °C. Samples were submitted to the Biogeochemical Analytical Service Laboratory at the University of Alberta for analyses of water quality parameters that included soluble reactive P (SRP), total dissolved P (TDP), total P (TP), total suspended solids (TSS) and dissolved organic carbon (DOC). In 2017, water samples were collected every third day during July and August and analyzed for only SRP.

Surficial sediment samples were taken four times over a two-week period in 2016 and three times over a nine-week period in 2017 to assess the spatial and temporal variability of surficial fine sediments. Representative samples of fine-grained surficial sediment were collected at each site using the method described by Lambert and Walling (1988) and then composited for each sampling period. This procedure involves placing a cylinder in the gravel-bed and agitating sediments to a depth of ~10 cm depth. The overlying water suspended sediment mixture was pumped into a triple-rinsed bucket and left to settle for two days. The water portion was decanted from the bucket and the remaining sediment was placed into ziplock bags, frozen and shipped back to University of Waterloo. Fine sediment samples were sieved to 250 μm and freeze dried for sorption experiments.

Representative samples of the gravel bed matrix were collected to a depth of 30 cm with a freeze-corer to determine the particle size distribution of the riverbed. Particle size distributions of the gravel bed matrix were evaluated using sieves. Each sample was weighed and shaken through a stack of large particle size wire sieves. Particles > 26 mm were measured manually and weighed individually. Samples were passed through 26 mm, 15.8 mm, 10 mm and 6.35 mm diameter sieves, and each retained sample was then weighed. A stack of mesh sieves, with 2 mm, 1.18 mm, 600 μm , 300 μm , 250 μm , 150 μm , and 63 μm diameters were placed in a sieve shaker for 10 minutes, removed and the mass in each sieve was weighed to determine the percent by mass for each size fraction. The freeze core samples were then sieved again to 250 μm and this material was freeze dried for sorption experiments to compare fine sediments within the top 30 cm relative to the top 10 cm surficial fine sediments. The remaining freeze core samples were used to calculate porosity by weighing the dried core, then saturating the sample and recording the saturated weight.

Dissolved Oxygen (DO) probes (ONSET U-26) were installed at the sediment-water interface (SWI) and at ~25 cm below the sediment water interface at each site. DO probes were calibrated and programmed to measure DO in ten minute intervals. Both the DO probes and PWPs were installed by removing the gravel (~25 cm deep) in the stream bed before placing the PWPs upright, and then immediately infilled with in-situ gravel. DO probes and PWPs were deployed for approximately 8 weeks in order to equilibrate.

3.3.3. Water chemistry and P sorption experiments

Water column samples were analyzed for concentrations of SRP in pore-water peeper samples were analyzed using ascorbic acid reduction colorimetric methods (Method G-175-96 Rev. 13; detection limit of $1 \mu\text{g P L}^{-1}$) with a Bran-Luebbe AutoAnalyzer III system multi-test MT18 in the Biogeochemistry Lab at the University of Waterloo. See Appendix B for QA/QC of pore-water concentrations.

The sorption kinetics between fine grained bed sediments and SRP in the water column of the Crowsnest River were investigated to provide simple estimates of SRP fluxes to/from the river bed sediments and overlying water column (Taylor and Kunishi, 1971; Froelich, 1988). Riverbed sediment samples collected from 6 sites, corresponding with increasing land disturbance sediment pressures were used to conduct batch experiments to determine the Equilibrium Phosphorus Concentration (EPC_0). The EPC_0 is a measure of the potential of sediments to adsorb or release SRP depending on the ambient SRP concentrations in aquatic systems (House & Denison, 1998; 2000). A 25 ml aliquot of phosphorus concentrations (0, 25, 50, 100, 200, 400 and $800 \mu\text{g P L}^{-1}$) was added in triplicate to 2.5 g of sediment in 50-mL centrifuge tubes. Centrifuge tubes were placed on the shaker table and shaken at 50 rpm at room temperature for 20-hours. An aliquot of 15-mL was filtered ($0.45 \mu\text{m}$) into scintillation vials and refrigerated. Concentrations of SRP were analyzed using ascorbic acid reduction colorimetric methods (Method G-175-96 Rev. 13; detection limit of $1 \mu\text{g P L}^{-1}$) with a Bran-Luebbe AutoAnalyzer III system multi-test MT18 in the Biogeochemistry Lab at the University of Waterloo for 2016. While 2017 samples were measured on a Technicon Autoanalyzer using the ammonium molybdate/stannous chloride method (Environment Canada, 1979). See Appendix B for QA/QC of EPC_0 experiments.

3.3.4. Estimating SRP diffusive flux across sediment-water interface

The diffusive flux of SRP at the sediment water interface was estimated using Fick's Law and SRP data collected from the pore water peepers. The diffusive flux uses the concentration gradient between sediments and the overlying water, distance and incorporates a diffusion coefficient. Net flux was calculated using the following equation:

$$F = \phi * D_0 * \left(\frac{\partial C}{\partial x} \right) \quad (1)$$

where F is the diffusive flux of phosphate ($\mu\text{g P m}^{-2} \text{d}^{-1}$) across the sediment-water interface (SWI), ϕ is the porosity of the riverbed, D_0 is the molecular diffusion coefficient for phosphate and $\partial C/\partial x$ is the concentration gradient between the maximum concentration in the top 5 cm of the sediment and the average P concentration 10 cm above the sediment-water interface. Porosity was calculated by:

$$\phi = \frac{V_v}{V_T} \quad (2)$$

where V_T is the total volume which was calculated using the mass of sediment divided by the density of silica (2.65 g cm^{-3}) and V_v is the volume of voids (the saturated weight minus the sediment weight).

To calculate the amount of phosphorus adsorbed the following equation was used:

$$P_{ads} = [(P_{initial} - P_{final}) * 0.025L] * wt_{sed}^{-1} \quad (3)$$

where P_{ads} = $\mu\text{g P}$ adsorbed per gram of sediment (dry weight), $P_{initial}$ = initial phosphate concentration ($\mu\text{g P L}^{-1}$), P_{final} = final phosphate concentration ($\mu\text{g P L}^{-1}$), and wt_{sed}^{-1} = weight of sediment (g).

3.3.5. Statistical Analyses

All statistical analyses were performed in R 3.4.3 (R Core Team, 2017). Non-parametric Mann-Whitney Rank Sum Tests were used to assess inter-site differences in 5 cm intervals of SRP pore-water concentrations and EPC_0 , due to the failure of these data to meet assumptions of normality. Overall differences in pore-water SRP concentrations between sites were assessed using Kruskal-Wallis Rank Sum Test. Linear regressions were performed to determine EPC_0 concentrations using batch isotherm data at each site and R^2 were calculated to assess the fit of the linear model.

3.3. Results

3.4.1. Porewater Soluble Reactive Phosphorus Concentrations and Fluxes

Pore-water SRP concentrations (median $5 \mu\text{g L}^{-1}$) ranged from 4 to $40 \mu\text{g L}^{-1}$, with one notable exception at S4A ($71 \mu\text{g L}^{-1}$) (Figure 3.3). Concentrations of SRP in pore-water peepers above the sediment-water interface were consistently around $5 \mu\text{g L}^{-1}$, except for at S5, which had SRP concentrations on the order of $10\text{-}30 \mu\text{g L}^{-1}$. Kruskal-Wallis analyses showed pore-water SRP concentrations varied between sites ($p < 0.01$). Post-hoc Mann-Whitney Rank Sum tests showed that site differences were largely driven by the higher pore-water SRP concentrations observed downstream of sewage inputs at S5 and S6. Site 5 was statistically different from all sites at all depths ($p < 0.05$), while site 6 was significantly different from sites 2 and 5 for all depths ($p < 0.1$) and below 20 cm depth S6 was significantly different from all sites ($p < 0.1$). Site 6 was the only site in which SRP concentrations increased with depth.

In general, SRP concentrations in the top 5 cm of sediment were different than the rest of the profile, and SRP was generally both larger and more variable in this sediment layer (Figure 3.3). The largest SRP concentrations and the greatest range of concentrations were measured in the top 5 cm below the SWI at Sites 1, 4, and 5 (wastewater effluent impacted). Increases in SRP at S1 were observed in the first 5 cm below the sediment water interface, however there were no statistical differences between S1 and other sites. Below a depth of 5 cm, SRP levels decreased and were more stable across most sites (particularly sites 2,3,4).

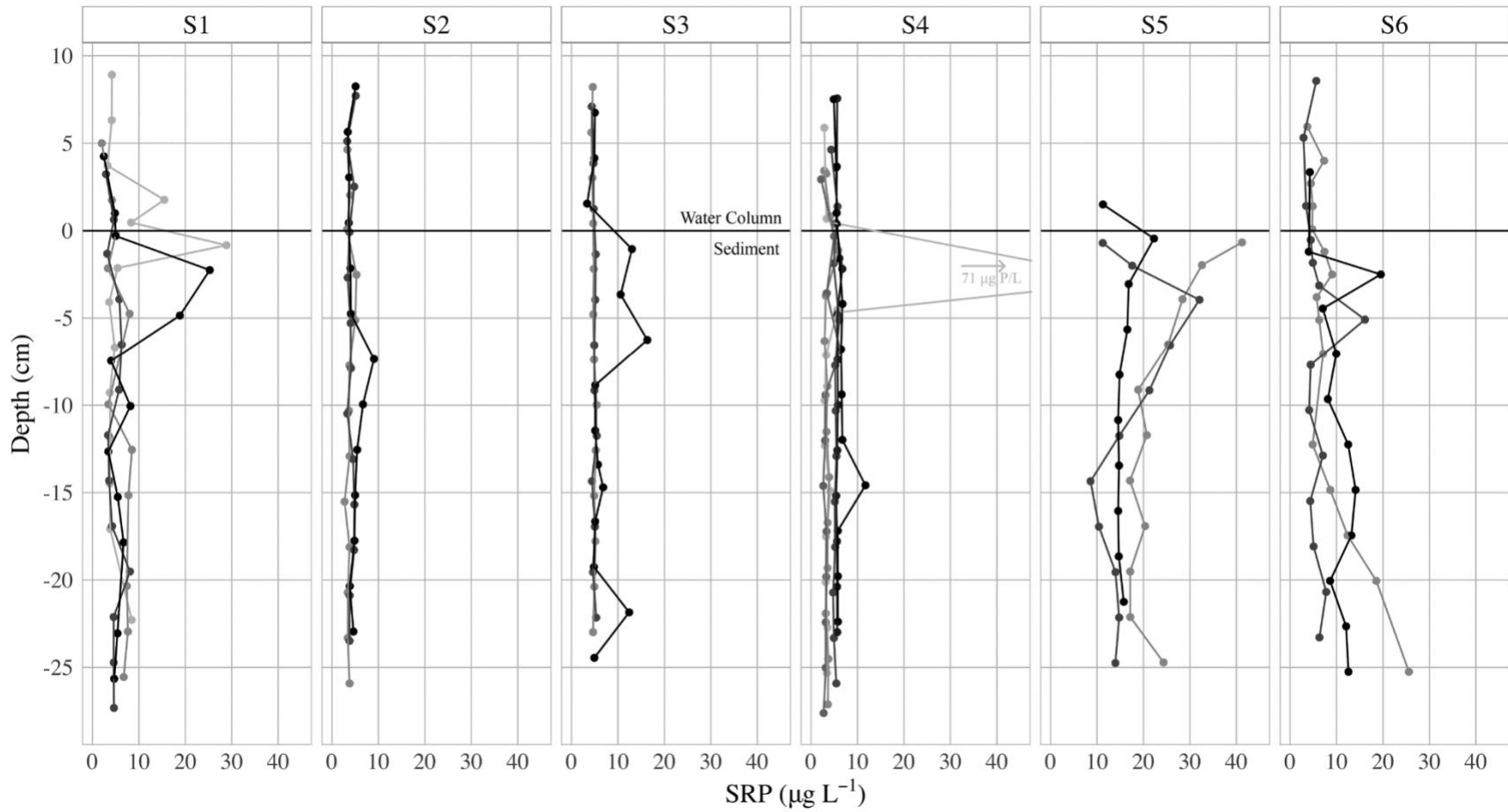


Figure 3.3. - The distribution of SRP with depth for porewater peepers placed in the gravel bed matrix (0 cm represents the sediment water interface) at six sites along the Crowsnest River. Each line represents a replicate at each site; three PWP's were placed at each site, with 4 at S1 and 6 at S4 (3 at the upper S4 location, 3 at the lower S4).

Potential daily fluxes of SRP from the sediment-water interface (Table 3.2) were generally low across the sites (0 to $-13 \mu\text{g SRP m}^{-2} \text{day}^{-1}$) with one notable exception at site 5 (median: $-6 \mu\text{g SRP m}^{-2} \text{day}^{-1}$). Although low, fluxes of SRP were consistently from the sediment to the overlying water (negative fluxes), except for at S2.

Table 3.2. - Soluble Reactive Phosphorus diffusive fluxes, calculated between average concentrations 5 cm below the SWI and 10 cm above the SWI, using Fick's Law, a diffusion coefficient of 6.12×10^{-10} and porosity. Negative values represent release from the riverbed to the water column.

Site	Rep	Daily Flux ($\mu\text{g m}^{-2}\text{day}^{-1}$)	Mean ($\mu\text{g m}^{-2}\text{day}^{-1}$)	Median ($\mu\text{g m}^{-2}\text{day}^{-1}$)
1	1	-1.5	-2.0 ± 2.2	-0.5
	2	-0.9		
	3	-0.3		
	4	-5.3		
2	1	-0.6	-0.1 ± 0.5	0.0
	2	0.3		
	3	0.0		
3	1	-0.1	-0.7 ± 1	-0.2
	2	-0.2		
	3	-1.9		
4A	1	-9.0	-3.3 ± 4.9	-0.8
	2	-0.4		
	3	-0.8		
4B	4	0.1	-0.1 ± 0.2	-0.1
	5	-0.1		
	6	-0.3		
5	1	-13.3	-7.9 ± 4.6	-5.5
	2	-5.2		
	3	-5.5		
6	1	-0.6	-0.7 ± 0.6	-0.6
	2	-0.3		
	3	-1.4		

3.4.2. Chemical conditions of the water column

During the study period, there was little variability in water column concentrations of SRP among the sites (Figures 3.4 and 3.5). SRP typically ranged from 1 to 7.5 $\mu\text{g L}^{-1}$. One notable exception was observed at Site 5, which receives inputs from a wastewater treatment plant (median 12 $\mu\text{g SRP L}^{-1}$, range 3 to 21 $\mu\text{g L}^{-1}$).

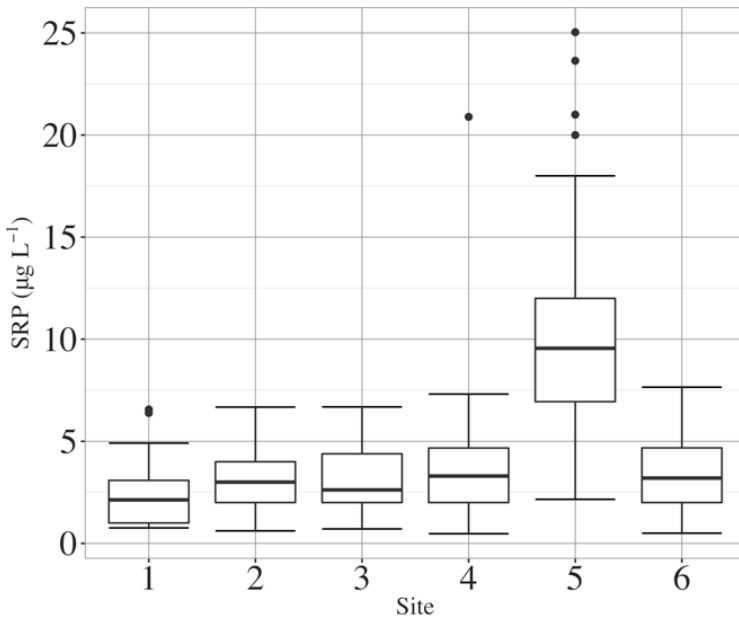


Figure 3.4. - Boxplots of SRP (n=40) for the 2016 and 2017 for the water column during low flow.

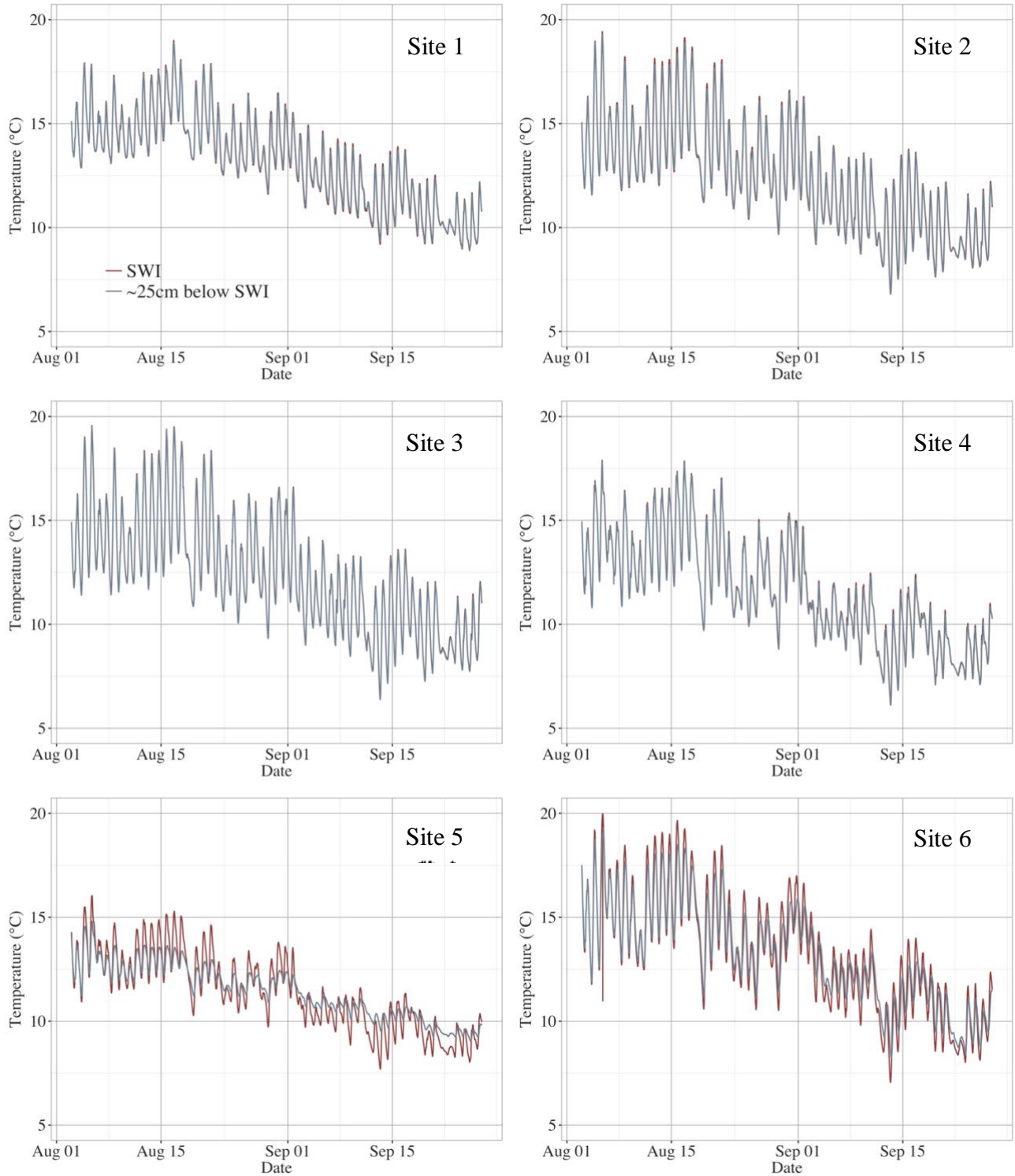


Figure 3.5. - Stream temperature of six sites along the Crowsnest River at the sediment-water interface (red) and ~25cm in the gravel bed matrix (dark grey).

Water column temperatures at the sediment-water interface along the Crowsnest River were fairly consistent across sites. Mean daily temperatures at the SWI varied between 11.4 and 13.3 °C (Sites 5 and 6, respectively), with average daily maximum temperatures between 12.5 (Site 5) and 15.3 °C (Site 1) and average daily minimum temperatures between 9.8 (Site 4) and 11.9 °C (Site 1). Sites 1, 4 and 5 experienced the least temperature variation at the SWI, while the smallest average diurnal ranges (average daily max – average daily min) at 25 cm in the gravel-bed matrix were observed at sites 1, 5 and 6 (see Figure 3.5 for differences in temperature within the gravel-bed at each site).

Inter- and intra-site variability in dissolved oxygen concentrations for all sites and depths along the Crowsnest River are presented in Table 3.3. These data are a proxy for redox conditions in the riverbed. DO concentrations patterns varied temporally and across sites. DO was lower at downstream sites 5 and 6, and the latter site had greater diurnal variability. DO concentrations at sites 5 and 6 were considerably lower at 25 cm depth compared to the SWI, with daily average concentrations of 0.1 mg L⁻¹ and 2.1 mg L⁻¹, respectively. Likewise, S1 also had lower DO concentrations at 25 cm depth compared to SWI DO concentrations. In contrast, DO concentrations were greatest at Site 3 and did not differ between the two depths.

Table 3.3. - Daily averaged dissolved oxygen concentrations (mg L⁻¹) for the sediment-water interface and approximately 25 cm below the sediment water interface at six locations along the Crowsnest River, AB

Site	Sediment-water interface probe			~25 cm below sediment-water interface		
	Average Daily DO Max	Average Daily DO Min	Daily DO Average	Average Daily DO Max	Average Daily DO Min	Average Daily DO
1	9.7	7.8	8.8	9.0	7.1	8.0
2	8.1	6.2	7.1	9.8	7.8	8.8
3	10.6	9.0	9.8	10.5	8.8	9.7
4	9.8	7.6	8.8	10.0	7.9	9.1
5	5.5	3.7	4.7	0.3	0.0	0.1
6	5.3	1.5	3.3	4.8	0.2	2.1

The particle size distribution and porosity of the riverbed sediment at each site are depicted in Figure 3.6 and Table 3.4, respectively. Porosity, a measure of the proportion of water in the gravel matrix, was relatively similar across sites, ranging between 30 and 41%. However, the size distribution of sediments varied across sites, with the smallest D_{50} at S4A (2.6 mm) and the largest D_{50} (27.5 mm) at 4B. Sites 3 and 5 also had relatively small D_{50} values, around 10-11 mm. These data highlight differences between subsurface material and its potential influence on flow paths and solute transformations (Boano et al., 2014).

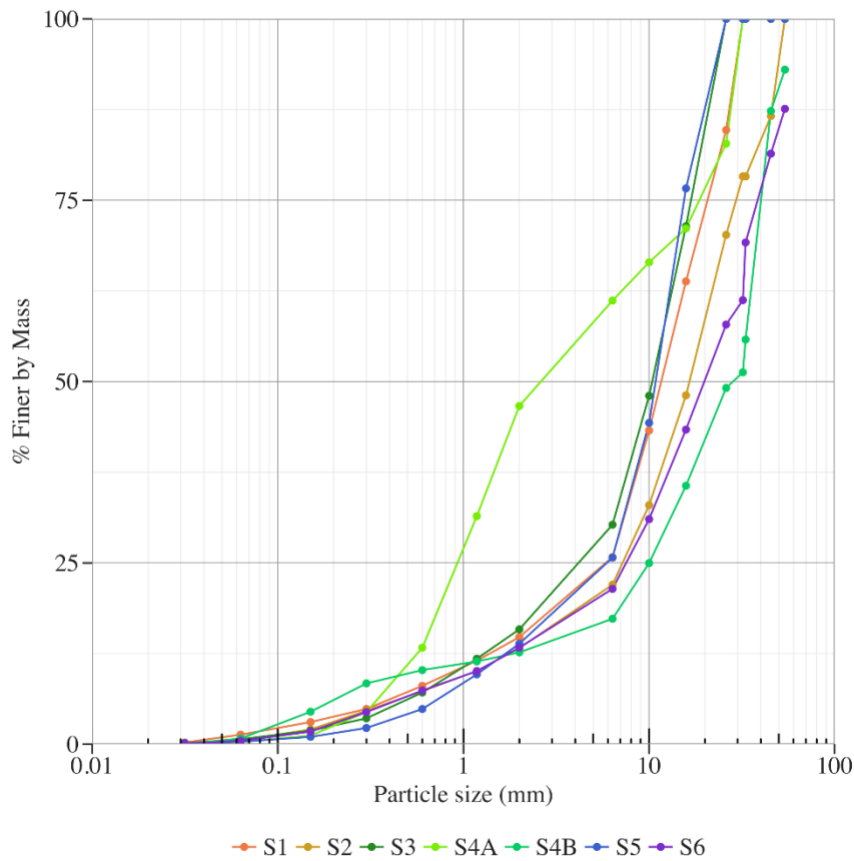


Figure 3.6. - Cumulative particle size distribution of river bed sediment in the Crowsnest River

Table 3.4. - Physical properties of riverbed at each site

Site	Porosity (%)	D ₅₀ (mm)	% finer than 300 µm	Mass finer than 300 µm (g)
1	38	11.7	4.9	18.9
2	32	17.5	4.6	35.8
3	36	10.3	3.6	27.6
4A	34	2.6	4.4	75.5
4B	35	27.5	8.4	22.1
5	41	10.9	2.2	18.2
6	30	19.9	4.4	44.8

3.4.3. Temporal and Spatial Variability in Sorption Dynamics

Inter- and intra-site variability in the EPC₀ illustrate the complex nature of sorption characteristics at micro- and macro-site scales along a river (Figure 3.7). There was no clear spatial pattern in EPC₀ as a function of distance downstream or disturbance type. Median EPC₀ concentrations were greatest at sites S1 and S5 and smallest at S4B and S2, with intermediate concentrations at sites 3, 4A and 6. EPC₀ concentrations were relatively consistent at sites 2 and 4A (Figure 3.7), while the ranges of EPC₀ concentrations were larger at other sites.

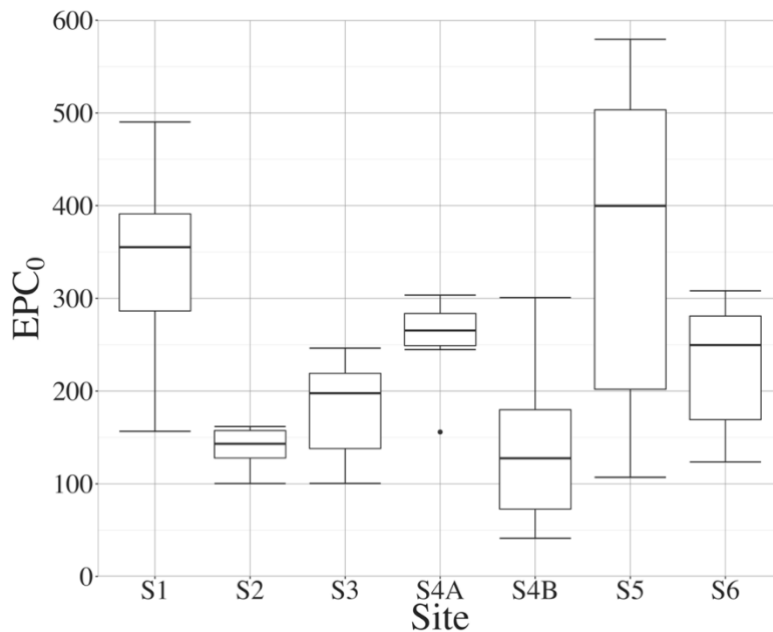


Figure 3.7. - EPC₀ for six sites (n=7 per site) along the Crowsnest River in 2016 and 2017.

EPC₀ concentrations of surficial sediments (top 10 cm) varied considerably across a reach (Figures 3.8 and 3.9), see Appendix A, table A3 for EPC₀ regressions. Sorption characteristics (y-intercept and slope) were more variable at sewage impacted sites. All surficial sediments demonstrated the ability of fine sediments to desorb P to the water column as EPC₀ concentrations were all significantly higher than water column concentrations. Fine sediments in the top 30 cm of the gravel-bed consistently had lower EPC₀ concentrations across sites compared to surficial sediments. In 2017, sediment samples were collected every three weeks over a 9-week period. There was no clear temporal pattern during this low flow period, however the same variable patterns were observed for surficial sediments.

EPC₀ concentrations were higher at site S1 compared to all other sites except for at sites 4A and 5 ($p \leq 0.05$). Similar to site 1, site 5 below the sewage outfall was highly variable across space and time, which was evident during a two-week sampling period and sampling every three weeks over a 9-week period. The greatest variability in EPC₀ was observed below the sewage outfall and because of this variability the only statistically significant differences were observed between site 5 were S2 and S4B ($p < 0.05$). This same pattern was observed for sites 6 and 4A ($p < 0.1$), with S4A having a greater EPC₀ than S3. Site 2 had the lowest average EPC₀ concentration which differed significantly from all sites except S4B and S3 ($p < 0.05$).

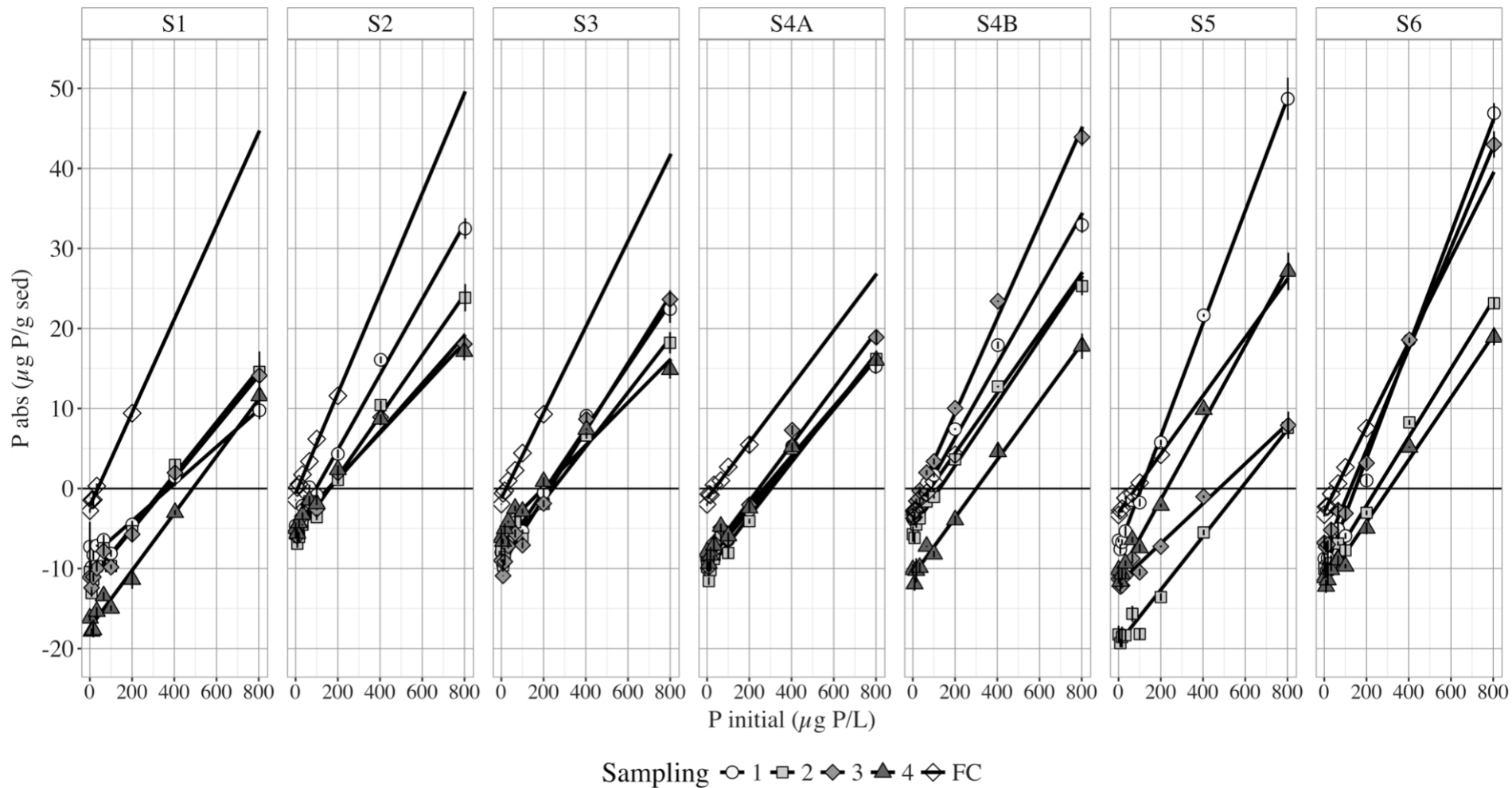


Figure 3.8. - Batch isotherm experiments for 4 different surficial (0-10 cm depth) fine sediment riverbed samples collected within a two-week period at six sites along the Crowsnest River in mid-August of 2016. Freeze core (FC) samples batch isotherms are representative of fine sediments collected from 0-30 cm depth.

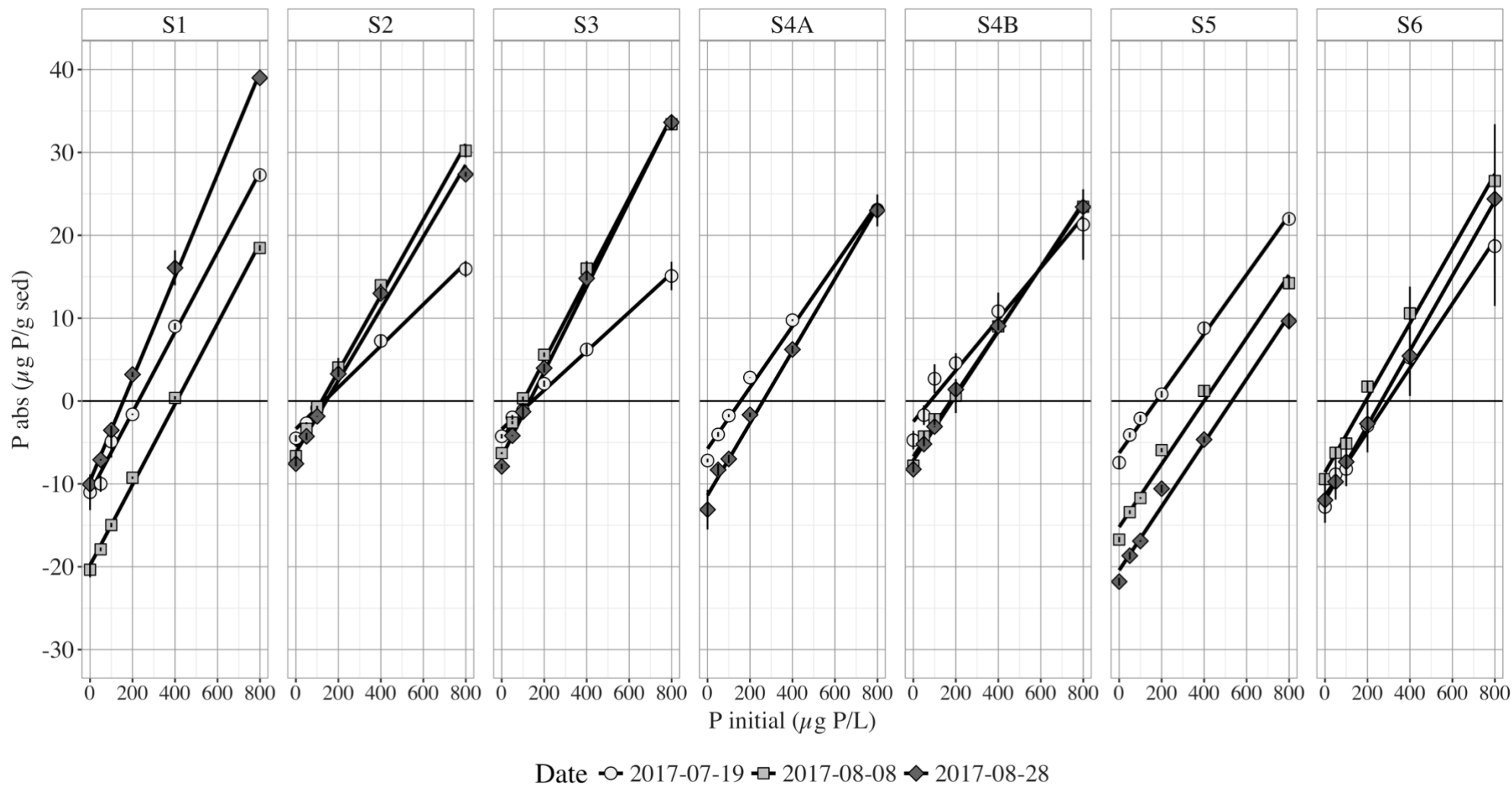


Figure 3.9. - Batch isotherm experiments for different surficial (0-10 cm depth) fine sediment riverbed samples collected approximately every two-week at six sites along the Crowsnest River between July and August of 2017.

3.5. Discussion

3.5.1. Porewater SRP concentrations and fluxes

In the Crowsnest River SRP pore-water concentrations were higher than in the overlying waters. Overall, pore-water SRP concentrations were $< 10 \mu\text{g L}^{-1}$, which is considerably lower than what has been reported for rivers with finer textured sediments impacted by agriculture and sewage effluent (Reddy et al., 1996; Jarvie et al., 2008). Indeed, a wide range of riverbed pore-water SRP concentrations using a range of methods have been reported in the literature. For example, pore-water SRP concentrations $> 10 \text{ mg L}^{-1}$ were reported in sewage impacted rivers in eastern England (Palmer-Felgate et al., 2009). In agricultural streams, Burns et al., (2015) reported pore-water SRP concentrations of $\sim 3.5 \text{ mg L}^{-1}$. In contrast, much lower values are reported for undisturbed systems, for example, in the Pembina River in Alberta average pore-water SRP concentrations ranged between 70 and $\sim 440 \mu\text{g L}^{-1}$ (Chambers et al., 1992). The previous examples were all from studies conducted in riverbeds with finer particle size distributions (e.g. sand riverbeds), with the exception of the Pembina River where the bed substrate varied between fine sediment and cobbles. However, higher diffusive fluxes of SRP in the Crowsnest River below sewage outfall are comparable to an armored gravel site in an intensively agricultural area the UK (Jarvie et al., 2008). Moreover, pore-water diffusive fluxes were considerably lower than fluxes observed in lakes, reservoirs and estuaries (Table 3.5 – e.g., Teague et al., 1988), but lotic systems typically stratify and organic matter is usually derived from autochthonous sources (Simmons & Wallschläger, 2005) which suggests different biogeochemical processes could be driving fluxes. There is a paucity of data on pore-water fluxes from riverbeds; however available studies show that riverbeds can be either sources or sinks of P (Reddy et al., 1999; Jarvie et al., 2008; Table 3.5). While all fluxes in this study were relatively low, the P release to the water column was positive, demonstrating that P is supplied to the water column, which can influence the benthic community particularly in this typically oligotrophic system (Silins et al., 2014).

Table 3.5. - Pore-water fluxes to overlying water values ($\mu\text{g SRP m}^{-2} \text{ day}^{-1}$) in the literature, across a variety of landscapes. Negative values represent fluxes to the water column from sediments, positive values represent adsorption to sediments.

Descriptive variables					Daily Flux ($\mu\text{g SRP m}^{-2} \text{ day}^{-1}$)	
Citation	Location	Impacts	Type	Site	Min	Max
This study	Alberta, Canada	Wildfire, sewage	River	Crowsnest River	0	-13
Reddy et al. 1996	Florida, US	Dairy/pasture, stream channelization	River	Otter Creek	+2500	-7700
Jarvie et al. 2008	SE UK	Intensive arable farming	River	Eye Brook (Armoured gravel)		-13
	SE UK	Intensive arable farming	River	Eye Brook (Fine sediment)	+66	
Kleeberg et al. 2010	Germany	Urban	River	Spree River	-40	-210
Urban et al. 1997	Switzerland	Agriculture, historic sewage	Lake	Lake Sempach	-2478	-6195
Moore et al. 1998	Florida, US	Agriculture, urban	Lake	Lake Okeechobee		-1000
Zhao et al. 2017	China	Cropland, industry and wastewater	Lake	Ulansuhai Lake	+92	-53
Chowdhury and Bakri 2006	Australia	Urban	Reservoir	Suma Park	-50	-220
Teague et al. 1988	Louisiana, US	Surrounded by saline marshes	Estuary	Atchafalaya-Fourleague Bay	+37164	-13379
Lavery et al. 2001	Australia	Intensive urban	Estuary	Swan–Canning	-500	-53000

Inter- and intra-site variability of pore-water SRP concentrations and fluxes in the Crowsnest River demonstrate that disturbance impacts are a product of landscape type and disturbance as well as in-stream substrate heterogeneity, which may influence the mobility of P in gravel-bed systems. The greatest differences in SRP at the sediment-water interface (SWI) were observed downstream of primary treated sewage effluent (S5) and interestingly at the most upstream location S1 (reference site). The S1 site was the most upstream and least impacted site; however, the significant growth of *Didymosphenia geminata* observed across the entire reach suggests that the presence of biofilms can influence the permeability of the reach resulting in higher diffusive fluxes (Woodruff et al., 1999; Pintelon et al., 2012; Battin et al., 2016). There was no clear pattern in pore-water SRP gradients and pore-water peepers exhibited variability across triplicates at each site. This suggests that micro-site differences may influence pore-water SRP concentrations and fluxes. For example, at site 4, both of the finer and coarse substrate locations had low pore-water concentrations, but the finer substrate had slightly higher fluxes. Bardini et al., (2013) demonstrated the limited influence of the permeability of riverbeds on nutrient cycling in lowland rivers, however this study brings into question the validity of this assumption is for gravel-bed systems where greater variability in grain-sizes is possible. While inter-site variability is likely driven by sediment sources and disturbances, intra-site variability in pore-water SRP concentrations and fluxes suggests that different sensitivities to disturbance is a product of site specific factors, such the heterogeneity in gravel-bed substrates and ecological communities.

3.5.2. Equilibrium Phosphorus Concentrations

The EPC_0 of sediment has been widely used to quantify the abiotic control of sediment to govern P dynamics (uptake of release) in aquatic systems (e.g., Froelich et al., 1988; McDowell, 2015; Emelko et al., 2016; Table 3.6). However, assessments of riverbed sediments to regulate P dynamics have been primarily conducted in systems impacted by anthropogenic (urban and agriculture) sources (e.g., House & Denison, 2002; McDowell & Sharpley, 2003; Jarvie et al., 2005; Agudelo et al., 2011; McDowell et al., 2015). High EPC_0 values ($>1 \text{ mg L}^{-1}$) for riverbed sediments have been observed in an intensive agricultural system (Agudelo et al., 2011) and in a river system impacted by wildfire (Son et al., 2015). The methods for determining EPC_0 varies considerably across the literature, and therefore, caution should be used when comparing EPC_0

Table 3.6. - EPC₀ concentrations ($\mu\text{g L}^{-1}$) for different riverbed sediments across a variety of landscapes and impacts

Citation	Location	Impacts	Site	Min EPC ₀	Max EPC ₀
This study	Alberta, Canada	Wildfire, sewage	Crowsnest River	41	579
Klotz 1988	New York, USA	Headwater	Hoxie Gorge Creek	<1	2
Stutter and Lumsdon 2008	NE Scotland	Moorland, bog, grassland, forest plantations	River Dee	1	54
Reddy et al. 1996	Florida, US	Dairy farms/pasture	Otter Creek	120	230
McDowell and Sharpley 2003	Pennsylvania, USA	Majority agriculture	Manhantango Creek	11	39
Jarvie et al. 2005	SW UK	Agriculture, pasture, grazing	Avon	2	178
Jarvie et al. 2005	SW UK	Agriculture, pasture, grazing	Wye	<1	195
House and Warrick 1999	NE England	Pasture, tributary with sewage impact	Swale River	1	55
Palmer-Felgate et al. 2009	Southern UK	Differing agricultural intensity	Avon/Wye/Welland	2	79
Hoffman et al. 2009	Wisconsin, USA	Agriculture	Dorn Creek	6	71
Machesky et al. 2010	Illinois, USA	Agriculture	Spoon River	6	68
Agudelo et al. 2011	Kansas, USA	Intensive agriculture	Upper West Emma Creek/Red Rock Creek	800	1300
Ekka et al. 2006	Arkansas, USA	WWTPs, agriculture, pasture	Illinois River	<10	290
House and Denison 2002	Southern UK	Sewage	River Blackwater	6	610
Wang and Pant 2015	NY, USA	WWTP, stormwater, urban	Bronx River	20	730
McDowell et al. 2015	New Zealand	Differing impacts	National scale study (76 sites)	7	100
Son et al. 2015	Colorado, USA	Wildfire	Cache la Poudre River	30	1200

values. EPC_0 values for the Crowsnest River are comparable to those reported rivers impacted by urbanization and agriculture (Table 3.6). Accordingly, data in the present study suggests that fine material found in the Crowsnest River which is typically oligotrophic system has considerable potential to release P to the water column.

Some studies have been able to correlate EPC_0 with SRP concentrations in the water column during low flow (Klotz et al., 1988; McDowell et al., 2003). However, in the present study, intra- and inter-site variability were great across both years, which brings into question the reliability of large scale assessments of P mobility and suggests the predictive limitations of correlations between EPC_0 and low flow SRP concentrations for gravel-bed rivers. In addition, fine sediments throughout the top 30 cm of the sediment profile typically desorbed less P to the water column, suggesting distinct differences with surficial sediment properties. This difference in surficial sediments could be due to the different physical, chemical and biological properties of this material (Stone & Droppo, 1994). Overall, within a gravel-bed river, over time, across a reach, and along a downstream gradient, there was large variability in EPC_0 which brings into question the validity of point sampling of EPC_0 for the assessment of ecosystem health. The variability and magnitude of EPC_0 values varied within and between sites in the Crowsnest River highlight the diverse pathways of biogeochemical processes that influence solubility of P.

Fine sediments in the Crowsnest riverbed were a source of P to the water column during low flow in this typically oligotrophic river system. Physical and biogeochemical factors that affect EPC_0 include sediment size (Stone & English, 1993; Gainswain et al., 2006), mineralogy (House & Denison, 2002; Withers & Jarvie, 2008), contact time, sample to solution ratio (Bhadha et al., 2012) and solution chemistry (Lucci et al., 2010). Therefore, EPC_0 concentrations in the Crowsnest River are likely imprecise, however EPC_0 concentrations were all at least an order of magnitude greater than the surface water concentrations, therefore fine riverbed sediments in the Crowsnest River still act as a significant source of SRP to the water column. Moreover, sites impacted by sewage (Site 5) and presence of biofilms (Site 1) demonstrated great potential of sediment to desorb P to the water column. In a study of two sand/silt rivers that were heavily impacted systems (sewage/agriculture), Jarvie et al. (2005) reported that water column SRP concentrations were highly variable as a function of seasonal flow events, yet EPC_0 concentrations of riverbed sediment were relatively consistent within seasons (Figure 3.10). The relatively recent disturbances in the Crowsnest River compared to the longer historical impacts in rivers documented by Jarvie et al.

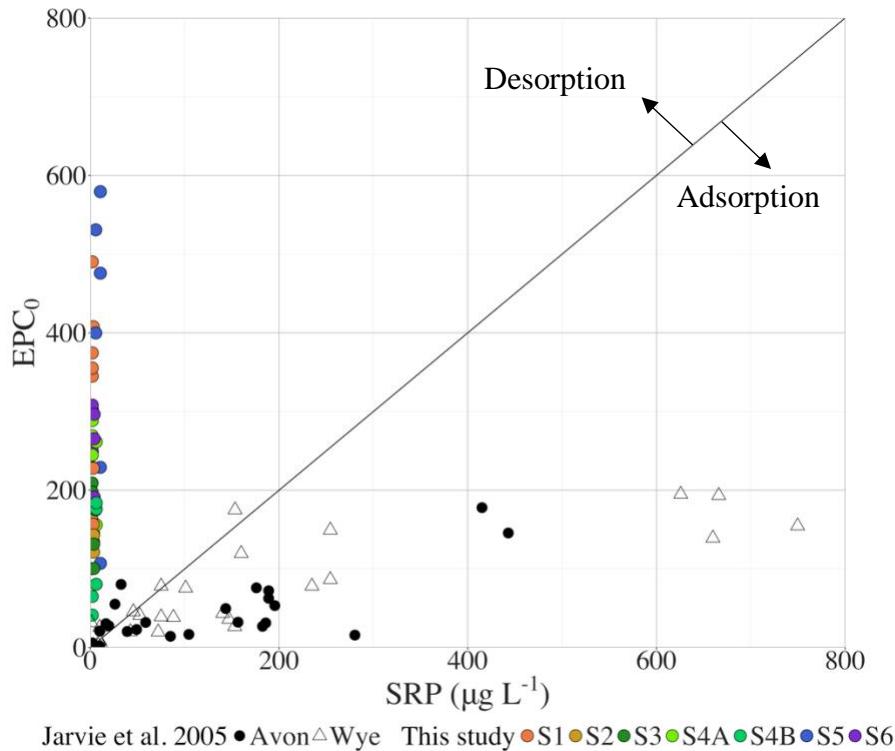


Figure 3.10. - EPC₀ concentrations in relationship to water column concentrations for the Crowsnest River (this study) and two impacted rivers (by sewage and agriculture), the Avon and Wye (Jarvie et al., 2005).

(2005) could explain the difference in this variability. While SRP concentrations in the Crowsnest River did not fluctuate much during the low flow period, EPC₀ was found to vary considerably across sites. For instance, below the sewage outfall EPC₀ concentrations ranged between ~100 to ~600 µg L⁻¹ and site 1 (with *D. geminata*) ranged between ~150 and ~500 µg L⁻¹. Jarvie et al. (2005) sieved sediment samples to a larger grain size (<2 mm) and mimicked stream water chemistry, using a CaCl₂ solution to match conductivity and calcium concentrations, and temperatures. Accordingly, higher EPC₀ concentrations and variability measured in the Crowsnest River relative to those reported by Jarvie et al. (2005) could be due to differences in substrate size and experimental methods. Regardless, the range of EPC₀ in the Crowsnest River relative to the Avon and Wye Rivers (Table 3.6) suggest that the heterogeneous nature of gravel-bed rivers provides a range of ingress opportunities that create large variation in amount and nature of fine sediment within different disturbances and therefore different sensitivities to landscape impacts.

3.5.3. Controls on P mobility in the gravel-bed matrix

The residence time of water in the gravel matrix tends to increase with decreasing substrate porosity which can affect the contact time of water with sediments and ultimately solute transformations (Bardini et al., 2012). In the present study, porosity across sites was relatively similar; however, the particle size distributions varied, which can also be an indicator of permeability and residence times (Findlay, 1995). In study of a tributary to the Welland River in the UK, Jarvie et al. (2008) observed a part of the bed with fine sediment was adsorbing P, while fine sediments within armored gravel released P. The authors suggested that colmation of fine sediments in gravel can be a source of P. Retention and colmation of fine sediments within the riverbed can depend on the particle size distribution of the riverbed, (Carling, 1984). In the Crowsnest River, impacted sites that had a greater frequency of smaller pebbles (i.e. smaller D_{50} of riverbed substrate) had increased pore-water SRP concentrations at the sediment-water interface (i.e., S4A, S5) which could be a result of fine sediment distributions, permeability and residence times. Additionally, in areas with reduced permeability or biofilm formation, as seen at the most upstream site in the Crowsnest River, flow can be impeded and result in a deposition of surficial fine-grained laminae (Stone & Droppo, 1994; Battin et al., 2003) that can create a distinct P gradient across the sediment-water interface (Dorioz, 1996). Higher EPC_0 in surficial sediment at sites 1, 4A, and 5 may have reduced water fluxes across the sediment-water interface because of biofilms and smaller grain sizes, which could partially explain the observed higher concentrations of sediment-water interface pore-water samples. These observations suggest that the degree of heterogeneity of materials in the riverbed can strongly influence the rates of uptake and release of SRP from the sediment (i.e, source or sink).

Although not measured in this study, the amount and distribution of fine sediments at the sediment-water interface and subsurface flow may account for observed differences in SRP porewater concentrations (Duff & Triska, 2000; Boano et al., 2014). Kurz et al. (2015) found that diffusion was important for low permeability sediments where surface waters bypassed the hyporheic zone which resulted in a large chemical gradient. This study found that fluxes were stronger where permeability was reduced (inferred from grain size and presence of biofilms), this could be a product of methodology. Many studies (e.g., Reddy et al., 1996; Jarvie et al., 2008) have used porosity factors and assumed diffusivity, transferring methods from marine/sand-silt

systems. Future research should explore nutrient fluxes in turbulent systems by coupling tracer experiments, subsurface flows and pore-water concentrations. Given that PWP in the Crowsnest River were placed in areas (tail-end of pools) that are more likely to be down-welling and therefore oxic (Hendricks and White, 2000), the measured P fluxes may underestimate diffusive fluxes in other locations of the stream. Different results may have occurred if study sites were selected in slower moving portions of the river where upwelling is more likely (Hendricks & White, 2000; McClain et al., 2003).

Environmental conditions such as redox conditions and temperature in rivers can influence the mobility of P from sediments to the water column (House et al., 2003). Temperature can influence the precipitation of P with calcium and can reduce biotic activity of P cycling (House, 1999). Temperatures were relatively consistent across sites and depths, except for at site 5. In the Crowsnest River, temperature differences between the SWI and ~25 cm below the SWI were observed below primary sewage effluent at S5. Temperatures measured at ~25 cm below the SWI at S5 show that there is less attenuation of the diurnal amplitude than for other sites (see Figure 3.5). Accordingly, this suggests that either groundwater upwelling (Briggs et al., 2012) or colmation of surface sediments which reduces permeability (Veličković, 2005) which is further supported by low oxygen levels ($\sim < 1 \text{ mg L}^{-1}$) at ~25 cm below the SWI. Some studies have observed concurrent anoxic and oxic zones across a reach and related these spatial differences to availability of organic matter (Arnon et al., 2007). In this study, anoxic conditions ($< 0.5 \text{ mg DO L}^{-1}$) were observed during the diurnal cycle at sites 5 and 6, which suggest that dynamic anoxic conditions are present that may explain the presence of higher pore-water SRP concentrations at these sites. Under anoxic conditions SRP may be released from metal oxides (Mortimer, 1941), which could suggest that reduction of metals in the Crowsnest River are driving SRP release to pore-water. Accordingly, locations in the Crowsnest River that receive sediments that are more saturated with P and that are low in oxygen can likely be a greater source of SRP to pore-water and overlying waters.

3.6. Conclusions

A study was conducted to determine the abiotic control of fine sediment on phosphorus mobility in a gravel bed river with increasing land disturbance pressures during an environmentally sensitive period of summer low flow. The conclusions of the study are:

1. Pore-water in gravel beds is a source of P to the Crowsnest River.
2. SRP gradients across the sediment water interface were greatest at sites with smaller median grain size (D_{50}) and presence of biofilms.
3. Fine sediments stored in the gravel-bed demonstrated the ability to desorb P during ambient low flow water column concentrations at all sites.
4. Fine sediment at sewage impacted sites had the greatest and most variable potential to desorb P to the water column.
5. Both intra- and inter- spatial differences were observed with EPC_0 concentrations, highlighting the role of substrate heterogeneity in biogeochemical cycling of P within gravel-bed rivers.
6. Fine grained bed sediments stored in gravel beds will be entrained and transported to downstream environments (reservoirs) when river discharge is sufficient to move the amour layer. The potential release of P to the water column in reservoirs can enhance algal activity and lead to conditions that impact water treatability.

Chapter 4

Synthesis and Conclusion

Sediment is the primary vector for the transport of phosphorus (P) in terrestrial and aquatic systems and the type and distribution of particulate P forms (PP; NAIP, AP, OP) can strongly influence P dynamics in rivers (House, 2003). At increasing spatial scales, there are a range of physical, chemical and biological factors that influence P concentrations and cycling in rivers. Variable land disturbance coupled with complex surficial and underlying geology can lead to complex processes that affect P cycling (House & Denison, 2002; Stutter & Lumsdon, 2008; Records et al., 2016). Previous research on P dynamics has largely been conducted in river systems impacted by urban and agricultural land use (e.g., Vallet et al., 1990; Mulholland et al., 1997; Ballantine et al., 2009; Vervier et al., 2009) and typically there is less need to examine P dynamics in forested high quality source water regions. However, increasing attention is being directed towards understanding the effect of increasing sediment pressures from landscape disturbances on nutrient dynamics in oligotrophic river systems (Robson et al., 1996; Soulsby et al., 2002; Sosiak & Dixon, 2006; Smith & Owens, 2014) because increased nutrient availability in these sensitive streams can shift ecological communities (e.g., Silins et al., 2014) and have negative consequences to downstream water quality and water supply (Emelko et al., 2011). The overall goal of this thesis research was to examine the abiotic control of fine sediment on PP form and mobility in a low nutrient gravel-bed river experiencing cumulative effects of sediment and associated P pressures from land disturbance (roads, OHVs, stream crossings, harvesting, wildfire, and sewage effluent).

Particulate P in riverbeds can contribute significantly to P concentrations in the water column (e.g., McDowell & Sharpley, 2002), yet the storage and fate of PP is poorly understood. It remains unclear how PP forms change with different disturbances in conjunction with biogeochemical controls (Withers & Jarvie, 2008). In addition, few studies have rigorously examined the differences between PP in fine riverbed sediment and suspended sediments during the environmentally sensitive period of low flow (e.g., Owens & Walling, 2002). Indeed, there is a critical need to better understand sources of PP and the cycling of these P forms between sediment and overlying waters (House & Warrick, 1999; Jarvie et al., 2005; Stutter et al., 2007) as this period can favour biotic growth (Jarvie et al., 2002; Battin et al., 2003). Researchers have begun

to examine the role of riverbeds in P retention and hysteresis patterns (e.g., House & Warwick, 1998; Bowes et al., 2005; Jordan et al., 2005), but this work has largely focused on fine-grained (i.e., sand and silt) riverbeds. Gravel-bed rivers draining forested source water regions on the eastern slopes of the Rocky Mountains generally provide high quality water supplies (Bladon et al., 2014; Mahat et al., 2016). However increasing sediment pressures from landscape disturbance can degrade downstream water quality (e.g., Sosiak & Dixon, 2006; Silins et al., 2009; Bladon et al., 2014; Emelko et al., 2016). P cycling of fine sediment within gravel-beds has received little attention in the research community (e.g., Gainwain et al., 2006; Vervier et al., 2009), despite studies highlighting the importance of fine sediments clogging hyporheic zones and its impact on biogeochemical fluxes nutrient fluxes (Claret et al., 1997; Olsen & Townsend, 2003; Boano et al., 2014; Hartwig & Borchardt, 2014). Fine sediments have large surface areas per mass of sediment and metal oxide coatings (Horowitz & Elrick, 1987) that are largely associated with the labile fraction of P (Bostrom et al., 1988). As a result, fine sediments play an important role in buffer SRP and releasing SRP under reduction conditions (Stone & Mudroch, 1989). The present thesis fills this research gap by examining PP forms in suspended and fine riverbed sediments as a function of physical and geochemical properties across different sediment pressures in a gravel-bed river.

Geochemical properties of sediment and aqueous chemistry can control the sorption of P to sediment surfaces which is considered a primary control on surrounding aqueous SRP concentrations (Froelich, 1988). Moreover, due to the mixing of surface and groundwaters, the hyporheic zone is often considered a ‘hotspot’ for nutrient transformation and microbial activity (e.g., Bardini et al., 2012). Tracer and reach uptake studies have shown how P can be retained and have variable residence times within a reach depending on a range of physical and bio-geochemical factors. However, few studies in rivers have been conducted to rigorously characterize SRP concentrations and profiles in pore-water, the sediment water interface and the water column (e.g., Jarvie et al., 2008). Phosphorus sorption characteristics are often determined with the use of P isotherm experiments (e.g., Taylor & Kunishi, 1971; McDowell & Sharpley, 2003; Wang & Pant, 2010), where a known mass of sediment is mixed with a known concentration of SRP for a series of increasing SRP concentrations. The resulting data are used to interpret the buffer capacity of sediment and a point at which the sediment neither adsorbs nor desorbs P, defined as the ‘equilibrium P concentration’ (EPC_0) (Froelich, 1988). EPC_0 has been used as an index for

sediment pressures on P dynamics (e.g., Haggard et al., 1999; Agudelo et al., 2011; McDowell, 2015) but research has typically focused on single land-use impacts. While variability of sorption characteristics with laboratory methodology have been explored (e.g., Klotz, 1988; Lucci et al., 2010), variability of sediments within a reach and across multiple disturbances has received little attention. Accordingly, this thesis is the first to examine how pore-water SRP concentrations and fluxes vary in gravel-bed rivers as a function of environmental conditions (i.e., dissolved oxygen and temperature) with a range of cumulative landscape disturbance types. As well as, the inter- and intra-site variability of P mobility along this gradient is reported.

In this thesis, PP forms in the Crowsnest River were highly variable within and between sites that changed as a function of landscape disturbances. The Crowsnest River has a diverse surficial and bedrock geological setting which when combined with the complex nature of gravel-bed rivers, i.e., bed heterogeneity and morphology, demonstrated not only high intra- and inter-variability of PP bioavailability but differing degrees of sensitivity to landscape disturbances. The bioavailable PP form (NAIP) was significantly lower in fine riverbed sediments in contrast to suspended sediments. Sewage effluent greatly impacted the PP content and availability of suspended sediments and this finding supports the existing literature (e.g., Jarvie et al., 2005; Barral et al., 2012). Differences between fine riverbed and suspended sediments in the Crowsnest River were largely driven by higher concentrations of metal oxides, organic matter, specific surface areas and smaller particle size of suspended solids compared to fine sediment ingressed in gravel-beds. Apatite P (AP) was significantly greater in fine riverbed sediment, suggesting that differences in surface and subsurface water chemistry may have different controls on PP forms if different ions are present. The presence of organic carbon and redox-sensitive metals largely explained differences in NAIP forms as others have observed (e.g., Uusitalo et al., 2003; Ellison & Brett, 2006; Borch et al., 2010). These parameters were lower in the riverbed sediments which may be attributed to different grain sizes, differences in chemical and microbiological transformations, or different sediment sources from uniquely distinct geological bands that run perpendicular to the Crowsnest River. Cumulative effects of differing landscape disturbances on sediment associated P dynamics are difficult to assess due to uncertainty in apportioning landscape disturbance. Moreover, historical impacts, retention of sediments and the complex nature of heterogenous substrate and morphological features (pools, riffles) confound P dynamics. Overall,

landscape disturbances in conjunction with meso- and micro-scale processes can either attenuate or propagate P downstream.

Summer low-flows represent an ecologically sensitive period as increased nutrient availability can simulate primary productivity (Jarvie et al., 2005), therefore the understanding of within-streams P processes during this time is critical. This thesis shows that fine sediments and pore-water SRP concentrations can release SRP into the overlying waters regardless of landscape disturbance during low flow in this typically oligotrophic environment. Similar to PP forms, intra- and inter- site differences were observed with EPC_0 concentrations which suggests that micro- to macro- site processes need to be incorporated to understand P mobility at larger scales. Substrate heterogeneity impacted the biogeochemical cycling of P of this gravel-bed river, where SRP gradients were greatest at sites with smaller grain sizes or where the presence of biofilms could be impeding subsurface flow. Sites with lower dissolved oxygen concentrations within the bed had greater fluxes of SRP, which could be linked to smaller grain size and their influence on subsurface flow (Cardenas et al., 2004). Furthermore, fine sediment within 0-30 cm of the riverbed compared to fine sediment in the top 10 cm showed less potential to release P to the water column. This vertical difference could be the result of release, consumption or transformations of P that occur with longer residence times within the bed (Vervier et al., 2009). Sites downstream of sewage inputs had the greatest potential of fine sediment to desorb P to the water column, as well as the most variable impact to the water column. Lastly, fine sediment within the top 10 cm of the riverbed could represent a pool of P that when entrained and transported over time (years to decades) could influence the water quality and treatability of downstream reservoirs.

Particulate P forms and sorption characteristics of fine sediments demonstrate the interplay between macro- to micro-scale processes that influence downstream P cycling. These processes highlight the complexity of P dynamics in response to landscape disturbance and associated cumulative effects. Along the Crowsnest River between S2 to S4 varying degrees of disturbance from historic or contemporary harvesting, roads, stream crossings and off-highway vehicle use all confound the impact of recent harvesting and wildfire impacts and therefore cannot be assessed differentially. Fine sediment within the Crowsnest gravel-bed acted as a source of SRP to the surrounding aqueous environment during low flow, particularly downstream of sewage inputs. Suspended P content was typically lower at upstream sites (less disturbed) compared to below sewage effluent inputs, where P content and SRP fluxes from the gravel-bed were higher.

Moreover, the differences in PP forms between suspended and riverbed sediment could be a result of hyporheic modifications, as across sites apatite P was the dominant PP form in fine riverbed sediments. Particulate P forms were linked to sediment geochemistry in the Crowsnest River, while NAIP and EPC_0 were strongly correlated ($p < 0.05$), by extension, this suggests that sorption was largely driven by metal oxides. Given the link of bioavailable PP and metal oxides, it is not surprising that increased SRP fluxes were observed with lower oxygen concentrations. Overall, both PP form and sediment geochemistry influence the sorption of P, thus downstream impacts to P cycling and water quality will be strongly controlled by land-use, geology, morphology, substrate characteristics, sediment retention and local redox conditions.

The present thesis examined the intra- and inter- site variability of PP form and mobility across a downstream gradient with differing landscape disturbances, while this research provided knowledge to fill some gaps in the literature it also pointed towards the need for further research. For instance, heterogenous gravel-bed systems vary considerably in substrate and morphology which may differentially influence the rates and magnitudes of physical and biogeochemical controls on P cycling. As a result, future research should be cautious that point sampling could lead to inaccurate assessments of landscape disturbances. Furthermore, complex patterns of retention of P during low flow can confound the cumulative effects assessments of different landscape disturbances. Future studies should explore hotspots in gravel-bed substrate and morphology to better understand varying contributions to P cycling downstream. Similarly, coupling subsurface hydrology with PP and pore-water SRP could also provide insight into the transport and transformation of PP forms. Bioavailable forms of PP can act as a source of P, therefore improved understanding of how PP forms and sorption of P changes within the channel could benefit hysteresis studies of SRP. In order to understand P solubility sediment geochemistry needs to be related to surrounding aqueous chemistry. Lastly, the role of benthic biofilms and communities likely contribute to spatial variation in sediment sorption and PP forms, either through direct metabolism or indirect changes in subsurface flow and fine deposition, thus linking lentic fine sediment deposition and geochemistry with ecological communities will be important.

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Appendix A – Supplementary Information and Data

Photographs of Study Sites



Figure A1 – Most upstream site (S1), impacted by *Didymosphenia geminata*.



Figure A2 - *Didymosphenia geminata* diatom biofilm located at S1.



Figure A3 – Site 2 (S2) located below Allison Creek where there is an extensive ATV trail network.



Figure A4 – Site 3 (S3) located below Star Creek where a sub-catchment of this tributary has been harvested.

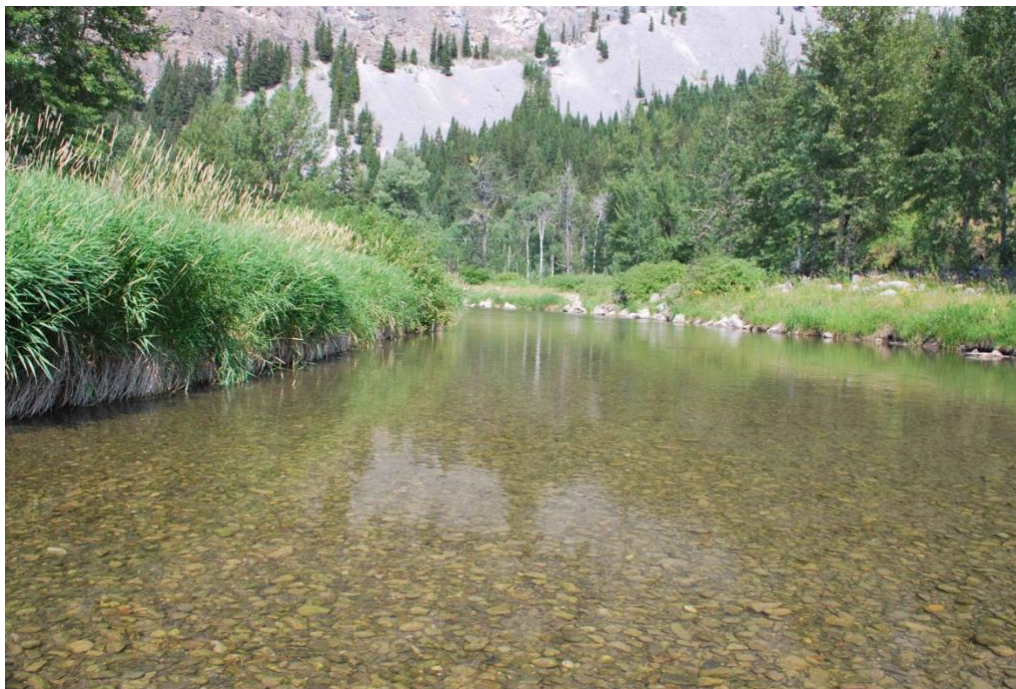


Figure A5 – Site 4A (S4A) located below Lyons Creek, a tributary that was burned in the 2003 Lost Creek Wildfire and salvage logged. S4A has a finer riverbed substrate.



Figure A6 – Site 4B (S4B) located below Lyons Creek, a tributary that was burned in the 2003 Lost Creek Wildfire and salvage logged. SB has a gravel/cobble riverbed substrate.



Figure A7 – Site 5 (S5) located below the Frank wastewater facility, and therefore sewage effluent inputs.



Figure A8 – Site 6 (S6) located ~25 km downstream of S5 and ~55 km downstream of S1, additional sewage inputs from the town of Hillcrest are ~15 km upstream and there is a small agricultural footprint.

Data

Table A1 - Major elements (averages \pm standard deviation) for fine riverbed sediment (< 250 μ m) collected within the Crowsnest River (2016-2017). For all major elements except for organic carbon n=7, organic carbon n=4)

Site	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Org C
S1	32.55 \pm 1.39	4.31 \pm 0.12	1.47 \pm 0.03	0.041 \pm 0.006	4.9 \pm 0.63	23.46 \pm 0.54	0.26 \pm 0.03	0.86 \pm 0.01	0.16 \pm 0.01	31.6 \pm 1.31	3.97 \pm 0.67
S2	65.35 \pm 1.88	5.81 \pm 0.44	2.16 \pm 0.14	0.031 \pm 0.008	2.3 \pm 0.04	8.23 \pm 0.48	0.49 \pm 0.01	1.18 \pm 0.09	0.17 \pm 0.01	13.28 \pm 1.46	1.83 \pm 0.32
S3	59.21 \pm 0.73	6.26 \pm 0.2	2.36 \pm 0.22	0.039 \pm 0.004	3 \pm 0.05	9.93 \pm 0.31	0.5 \pm 0.02	1.3 \pm 0.05	0.17 \pm 0.01	16.6 \pm 0.71	2.4 \pm 0.2
S4A	62.06 \pm 1.41	8.29 \pm 0.17	3.4 \pm 0.15	0.062 \pm 0.009	2.18 \pm 0.04	7.68 \pm 0.64	0.96 \pm 0.03	1.63 \pm 0.02	0.16 \pm 0.01	12.8 \pm 1.11	1.7 \pm 0.2
S4B	64.43 \pm 0.91	8.5 \pm 0.03	3.09 \pm 0.05	0.046 \pm 0.004	2.13 \pm 0.05	6.93 \pm 0.47	1.04 \pm 0.03	1.67 \pm 0.01	0.16 \pm 0.01	11.35 \pm 0.61	1.37 \pm 0.12
S5	64.18 \pm 0.44	8.92 \pm 0.06	3.52 \pm 0.27	0.054 \pm 0.004	1.92 \pm 0.02	6.29 \pm 0.27	1.08 \pm 0.03	1.74 \pm 0.01	0.17 \pm 0.01	11.23 \pm 0.76	1.47 \pm 0.21
S6	54.34 \pm 2.77	7.81 \pm 0.35	2.86 \pm 0.17	0.058 \pm 0.003	1.87 \pm 0.07	12.74 \pm 1.48	0.87 \pm 0.06	1.39 \pm 0.06	0.17 \pm 0	17.08 \pm 1.47	2.07 \pm 0.21

Table A2 - Major elements (averages \pm standard deviation) for suspended sediment collected within the Crowsnest River in 2016 (n=1).

Site	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	OC
S1	28.5	3.82	1.36	0.063	1.91	25.07	0.19	0.68	0.19	37.01	6.9
S2	52.23	7.32	2.76	0.059	1.95	9.22	0.3	1.52	0.2	22.65	4.4
S3	51.83	7.36	2.59	0.063	2.0	9.34	0.31	1.5	0.19	23.11	4.9
S4A	54.91	10.87	3.81	0.087	1.64	7.12	0.66	2.08	0.18	17.32	2.8
S4B	55.4	10.66	3.69	0.08	1.6	6.56	0.67	2.05	0.24	17.5	3.3
S5	42.37	9.23	3.26	0.097	1.64	14.81	0.43	1.67	0.21	24.51	3.7

Table A3 - Sorption isotherm linear equations and EPC₀ concentrations ($\mu\text{g L}^{-1}$) for fine riverbed sediment ($< 250 \mu\text{m}$) in the Crowsnest River (2016-2017). Samples from 2016 represent 4 separate samples taken over a two week period in early August, while 2017 samples represent samples taken approximate every three weeks between mid-July and late August. FC samples are fine riverbed sediment ($< 250 \mu\text{m}$) taken using a freeze core, representing 0-30 cm.

Site	Year	Sampling	Intercept	Slope	R ²	adj R ²	p	EPC ₀
S1	2016	1	-8.64	0.02	0.97	0.97	1.4*10 ⁻⁶	374.5
S2	2016	1	-4.75	0.05	0.99	0.99	1.8*10 ⁻⁸	100.3
S3	2016	1	-8.20	0.04	0.99	0.99	5.2*10 ⁻⁸	209.0
S4A	2016	1	-9.13	0.03	0.98	0.98	1.6*10 ⁻⁷	288.5
S4B	2016	1	-3.03	0.05	0.99	0.99	1.8*10 ⁻⁸	65.0
S5	2016	1	-7.52	0.07	1.00	1.00	1.9*10 ⁻¹⁰	107.0
S6	2016	1	-10.36	0.07	0.99	0.99	8.2*10 ⁻⁹	147.1
S1	2016	2	-11.17	0.03	0.97	0.96	1.5*10 ⁻⁶	344.9
S2	2016	2	-6.07	0.04	0.99	0.99	5.0*10 ⁻⁸	160.3
S3	2016	2	-8.36	0.03	0.98	0.98	1.9*10 ⁻⁷	246.3
S4A	2016	2	-10.28	0.03	0.98	0.98	2.1*10 ⁻⁷	303.5
S4B	2016	2	-5.02	0.04	0.99	0.99	3.2*10 ⁻⁸	127.5
S5	2016	2	-19.34	0.03	0.99	0.98	1.1*10 ⁻⁷	579.4
S6	2016	2	-10.67	0.04	0.99	0.99	8.5*10 ⁻⁹	249.6
S1	2016	3	-11.09	0.03	0.97	0.97	1.3*10 ⁻⁶	355.2
S2	2016	3	-4.84	0.03	0.98	0.98	1.9*10 ⁻⁷	161.7
S3	2016	3	-9.68	0.04	0.99	0.99	3.7*10 ⁻⁸	229.2
S4A	2016	3	-8.63	0.04	0.99	0.98	1.1*10 ⁻⁷	244.8
S4B	2016	3	-2.45	0.06	1.00	0.99	1.6*10 ⁻⁹	41.2
S5	2016	3	-11.85	0.02	0.98	0.98	1.2*10 ⁻⁷	475.8
S6	2016	3	-7.80	0.06	1.00	1.00	9.9*10 ⁻¹⁰	123.6
S1	2016	4	-18.85	0.04	0.94	0.93	1.4*10 ⁻⁵	490.2
S2	2016	4	-4.37	0.03	0.98	0.98	3.1*10 ⁻⁷	154.5
S3	2016	4	-5.29	0.03	0.98	0.97	6.7*10 ⁻⁷	197.7
S4A	2016	4	-8.34	0.03	0.99	0.99	5.4*10 ⁻⁸	269.1
S4B	2016	4	-10.90	0.04	0.99	0.99	1.3*10 ⁻⁸	300.9
S5	2016	4	-11.02	0.05	0.99	0.99	6.4*10 ⁻⁹	229.0
S6	2016	4	-11.99	0.04	0.99	0.99	1.5*10 ⁻⁸	308.2
S1	2016	FC	-2.18	0.06	0.99	0.99	2.6*10 ⁻⁶	37.0
S2	2016	FC	-0.62	0.06	0.99	0.99	3.9*10 ⁻⁶	9.9
S3	2016	FC	-1.22	0.05	0.99	0.99	3.4 *10 ⁻⁶	22.8
S4A	2016	FC	-1.24	0.03	0.97	0.96	6.1*10 ⁻⁵	35.5
S4B	2016	FC	-3.08	0.04	0.98	0.98	1.0*10 ⁻⁵	82.3

S5	2016	FC	-2.98	0.04	0.99	0.98	6.2*10 ⁻⁶	81.8
S6	2016	FC	-2.86	0.05	0.99	0.99	1.1*10 ⁻⁶	54.1
S1	2017	2017-07-19	-11.03	0.05	1.00	1.00	6.0*10 ⁻⁶	228.0
S2	2017	2017-07-19	-3.37	0.03	0.98	0.97	1.5*10 ⁻⁴	134.3
S3	2017	2017-07-19	-3.40	0.02	0.99	0.99	1.5*10 ⁻⁵	144.5
S4A	2017	2017-07-19	-5.76	0.04	0.99	0.99	2.1*10 ⁻⁵	155.9
S4B	2017	2017-07-19	-2.48	0.03	0.97	0.96	3.0*10 ⁻⁴	80.4
S5	2017	2017-07-19	-6.28	0.04	1.00	0.99	7.1*10 ⁻⁶	174.9
S6	2017	2017-07-19	-11.47	0.04	0.99	0.99	2.2*10 ⁻⁵	296.5
S1	2017	2017-08-08	-19.82	0.05	1.00	1.00	1.5*10 ⁻⁶	407.7
S2	2017	2017-08-08	-5.54	0.05	1.00	1.00	5.6*10 ⁻⁶	121.3
S3	2017	2017-08-08	-4.93	0.05	1.00	0.99	7.8*10 ⁻⁶	100.4
S4B	2017	2017-08-08	-6.70	0.04	1.00	1.00	5.0*10 ⁻⁶	175.9
S5	2017	2017-08-08	-15.21	0.04	0.99	0.99	5.0*10 ⁻⁵	399.8
S6	2017	2017-08-08	-8.61	0.05	0.99	0.99	1.4*10 ⁻⁵	191.3
S1	2017	2017-08-28	-9.65	0.06	1.00	1.00	6.5*10 ⁻⁷	156.6
S2	2017	2017-08-28	-6.21	0.04	0.99	0.99	2.7*10 ⁻⁶	143.1
S3	2017	2017-08-28	-6.75	0.05	1.00	1.00	2.6*10 ⁻⁶	131.5
S4A	2017	2017-08-28	-11.38	0.04	0.99	0.99	1.3*10 ⁻⁵	261.4
S4B	2017	2017-08-28	-7.16	0.04	1.00	1.00	5.0*10 ⁻⁶	183.9
S5	2017	2017-08-28	-20.43	0.04	0.99	0.99	4.3*10 ⁻⁷	530.9
S6	2017	2017-08-28	-12.00	0.05	1.00	1.00	1.3*10 ⁻⁷	265.4

Appendix B – QA/QC

Sorption QA/QC

Sample processing

Samples were freeze dried, ground and weighed out to 0.25 grams in polypropylene centrifuge tubes. Equilibrium experiments were performed by mixing weighed out samples with 25ml of 0, 25, 50, 100, 200 $\mu\text{g L}^{-1}$ KH_2PO_4 . Triplicate samples were done for each sample and concentration. Samples were shaken for 20 hours at room temperature of 24 ± 1 °C. Then samples were centrifuged at 4000G for 5 minutes, and the supernatant was filtered with 0.45 μm syringe filters.

The mass of inorganic P adsorbed or desorbed was determined using the following equation:

$$P_{\text{ads}} = [(P_{\text{initial}} - P_{\text{final}}) * 0.025\text{L}] * \text{wt}_{\text{sed}}^{-1}$$

Triplicate samples (separately weighed out samples) for fine riverbed sediments in the Crowsnest River had an average standard deviation of 0.6 $\mu\text{g P/ g}_{\text{sed}}$ (median: 0.4 $\mu\text{g P/ g}_{\text{sed}}$) in 2016, while samples from 2017 had an average standard deviation of 1.2 $\mu\text{g P/ g}_{\text{sed}}$ (median: 0.5 $\mu\text{g P/ g}_{\text{sed}}$).

AA Run

The following QA/QC is for colorimeter analysis of soluble reactive phosphorus. Samples from 2016 were run an AA3 channel using a Ascorbic Acid and Ammonium Molybdate method. While samples from 2017 were run on two AA2 channels using a Stannous Chloride and Ammonium Molybdate method.

Quality Cups and Drifts

Quality control cups for P concentrations of 10, 25, 50, 100 and 200 $\mu\text{g/L}$ were run in at least triplicate, longer runs had more quality cups. Drifts (300 $\mu\text{g L}^{-1}$) were placed evenly throughout each run. For each run all standard deviations fell below 5 $\mu\text{g L}^{-1}$.

AA sample triplicates

2016 samples

10% of samples (116 samples) were run in triplicate. The average standard deviation of samples run in triplicate was $2.7 \mu\text{g L}^{-1}$ (median: $1.7 \mu\text{g L}^{-1}$).

2017 samples

10% of samples (38 samples) were run in triplicate. The average standard deviation of samples run in triplicate was $7.9 \mu\text{g L}^{-1}$ (median: $4.3 \mu\text{g L}^{-1}$).

Pore-water SRP QA/QC

The following QA/QC is for colorimeter analysis of soluble reactive phosphorus. Samples were run an AA3 channel using a Ascorbic Acid and Ammonium Molybdate method.

Quality Cups and Drifts

Quality control cups for P concentrations of 0, 1, 5, 10, 25, and $50 \mu\text{g L}^{-1}$ were run 3 to 6 times, being evenly spaced throughout the run. The average standard deviation for quality cups was $0.6 \mu\text{g L}^{-1}$ (median: $0.3 \mu\text{g L}^{-1}$). Drifts ($100 \mu\text{g L}^{-1}$) were evenly spaced across the run, the standard deviation of drifts was $0.2 \mu\text{g L}^{-1}$ (n=37).

All samples were run in triplicate unless there was insufficient sample volume. The average standard deviation of samples run in triplicate was $1.3 \mu\text{g L}^{-1}$ (median: $0.1 \mu\text{g L}^{-1}$).

Phosphorus Speciation QA/QC

Aggregated samples from 2016 were run in triplicate for particulate P speciation. Total PP concentrations had a standard deviation of $10.5 \mu\text{g/g}_{\text{sed}}$ (median: $7.8 \mu\text{g/g}_{\text{sed}}$), NAIP concentrations had a standard deviation of $2.0 \mu\text{g/g}_{\text{sed}}$ (median: $2.2 \mu\text{g/g}_{\text{sed}}$), AP concentrations had a standard deviation of $8.5 \mu\text{g/g}_{\text{sed}}$ (median: $3.5 \mu\text{g/g}_{\text{sed}}$), and OP concentrations had a standard deviation of $1.8 \mu\text{g/g}_{\text{sed}}$ (median: $1.6 \mu\text{g/g}_{\text{sed}}$).